The 16th Annual Waste Testing & Quality Assurance Symposium

PROCEEDINGS

WTQA 2000

August 5-10, 2000

WPI
Waste Policy Institute
A Virginia Tech Affiliated Corporation

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Crystal Gateway Marriott ■ Arlington, VA

WTQA 2000

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Proceedings

The Sixteenth Annual

Waste Testing & Quality Assurance Symposium (WTQA 2000)

August 5-10, 2000

Crystal Gateway Marriott
Arlington, VA

HIGHLIGHTS

16th Annual Waste Testing & Quality Assurance Symposium (WTQA 2000) Environmental Sampling and Analysis in the 21st Century

Introduction

As we prepare to enter the 21st century it is appropriate to look forward and consider the changes that will affect environmental sampling and analysis over the next few years. Certainly advances in new technology will help to provide data that is sometimes more accurate, precise, faster, and cheaper (although not necessarily all of these improvements in any single method). In addition, we need to evaluate what policy-related changes will be wrought by NELAC and PBMS. Thus, we've organized a comprehensive program that focuses on these and related topics. This theme is also continued in the short course offerings. We invite you to join your colleagues from industry, government, and academia to contribute and learn from these discussions. Our goal is to enable you to take back to your work place a clearer understanding of how and where you can use forthcoming changes to improve your productivity.

The conference brings together regulators, analysts, engineers and managers from the Federal and State regulatory agencies, the regulated community and from the laboratory and engineering support communities in an informal setting on the edge of our nation's capitol.

The latest changes in regulatory policy, sampling techniques, and new methods will be presented and discussed. Formats include panel discussions, oral and poster presentations, and short courses. Topics include laboratory accreditation, compliance monitoring, facility compliance auditing, performance evaluation, method verification, laboratory and facility liability issues, the new proficiency testing program, in addition to the latest improvements in field and laboratory technologies and methods. Special issue sessions will focus on:

- **New Technologies Session 1 - Where is Technology Going in 2005?** The emphasis is on working smarter by taking advantage of new instruments, techniques, and sensors to get faster, cheaper, and better data.
- **New Technologies Session 2 - Business Ramifications.** How will new technologies affect the way business is conducted in the next 5 to 10 years?
- **Lab Accreditation Under NELAC.** B What are the changes in operations wrought by reciprocal accreditation, the new proficiency testing program, customer perception, and scientific misconduct?
- **Special Session - QA Then, Now, and Next.** Historical perspectives of past and present QA protocols with a focus on future changes being manifested by PBMS.

Program Highlights

Opening Plenary Session - ***Monday, August 7, 2000, 2:00 pm - 4:30 pm***
The plenary session features insights from top government officials and industry leaders. Presentations will range from new policy issues to the latest updates on progress and changes involving environmental monitoring and analysis.

Opening Reception concurrent with **Opening Tabletop Exhibition** - *Monday, August 7, 2000; 5:00 pm - 7:00 pm*
The opening reception follows the plenary session and is concurrent with the opening of the Tabletop Exhibition. Join us for complimentary hors d'oeuvres and soft drinks to meet your fellow conferees, exhibitors, and EPA officials. A cash bar will also be available.

Special Sessions
Special sessions on New Technologies and how they will impact environmental sampling and analysis in the near future are covered in two sessions. The first session is titled "Where is Technology Going in 2005?" Speakers in this session will emphasize how we can work smarter by taking advantage of new instruments, techniques and sensors to get faster, cheaper and better data. The second session is titled "Business Ramifications." Speakers in this session will share their perspectives on how the new technologies covered in the first session will affect the way business is conducted in the next five to ten years.

Two other special sessions will cover other current topics of interest. A session on "Lab Accreditation NELAC" will focus on the changes in operations that will occur from NELAC activities such as reciprocal laboratory accreditation by states, the laboratory proficiency testing program, and customer perceptions and concerns about scientific misconduct. The fourth special session is titled, "QA Then, Now, and Next." Historical perspectives of past and present QA protocols will be discussed with a focus on future changes being manifested by Performance Based Measurement System (PBMS).

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ORGANIC ANALYSIS

ORGANIC ANALYSIS

GROUND-WATER MONITORING: CAN IT BE AUTOMATED?

Scott Burge, Russell Burge and David Hoffman
Burge Environmental, 6100 South Maple, Suite 114, Tempe, AZ 85283

ABSTRACT

Current ground-water monitoring programs consist of manual sampling, disposing of purge water and analyzing the collected samples. Ground water monitoring is usually performed at less frequent intervals (i.e. quarterly) than may be desirable, because of the costs associated with long-term monitoring programs. In many cases, more frequent data could optimize a remedial action reducing clean-up costs. The long-term cost of monitoring ground water for sites subject to passive remediation can be significant using current protocols.

A successful automated monitoring system should contain the following components or modules: sampling, sensor, calibration, support, and control/data handling modules. A monitoring system should simulate a modern analytical instrument while remaining unattended in the field. The sampling module must be able to collect ground-water samples and place the analyte in a form which can be analyzed by the sensor module. The sensor module should have the specificity to detect a target compound at the low ppb (water) concentration range. The sensor should be located in a closed vessel that allows the introduction of either the sample or calibration standards. A sensor which cannot be calibrated would appear to be of limited usefulness in long-term ground-water monitoring. The calibration module should be designed to allow at least two to three concentrations (i.e. blank and known ppb) of analyte. The control/data handling module should be able to control the sampling, sensor and calibration functions, and acquire, process and transmit the signals from the sensor.

After several design changes it was decided that a single sensor should be allocated to each monitoring well or group of closely positioned wells. The monitoring system now being fabricated and tested by Burge Environmental has a sampling module capable of sampling up to eight intervals within an existing 4-inch (or larger) well and transporting the water samples to the sample module. The sensor which has been tested is a trichloroethene (TCE) specific optrode with a limit of detection of 2 to 5 ppb for most ground-water systems. The optrode uses a non-reversible reaction for the detection of TCE, however, the amount of reagent provided in the module will be capable of performing approximately 100 analyses before requiring a maintenance visit. The monitoring system was designed to accommodate other sensors as well as the TCE optrode. The optrode is calibrated with a system which injects methanol-based standards into the vessel enclosing the optrode. The sensor, calibration and control/data modules are located adjacent to the monitoring well. The system is battery operated and is recharged with solar cells. The only other support device which may be required is a source of compressed gas (small cylinder).

INTRODUCTION

An automated ground-water sampling system, based on our research, should contain five components or modules to be a successful long-term solution to monitoring ground water. The modules necessary for a ground-water monitoring system are:

- Sampling Module
- Sensor Module
- Calibration Module
- Support Module
- Control /Data Handling Module

The modules must be fully integrated and placed in a controlled environment in the vicinity of the water well to be monitored. Because of the need for periodic maintenance, significant differences in the design and construction of monitoring wells, and varying depths of ground water the monitoring system is placed into the ground adjacent to the monitoring well (Figure 1). This design allows for controlling the temperature of the monitoring system while providing easy access.

Sampling Module

The sampling module was designed specifically for interfacing with sensors mounted in or adjacent to the monitoring well. The sampling module is capable of collecting samples in as many as eight levels in a monitoring well allowing

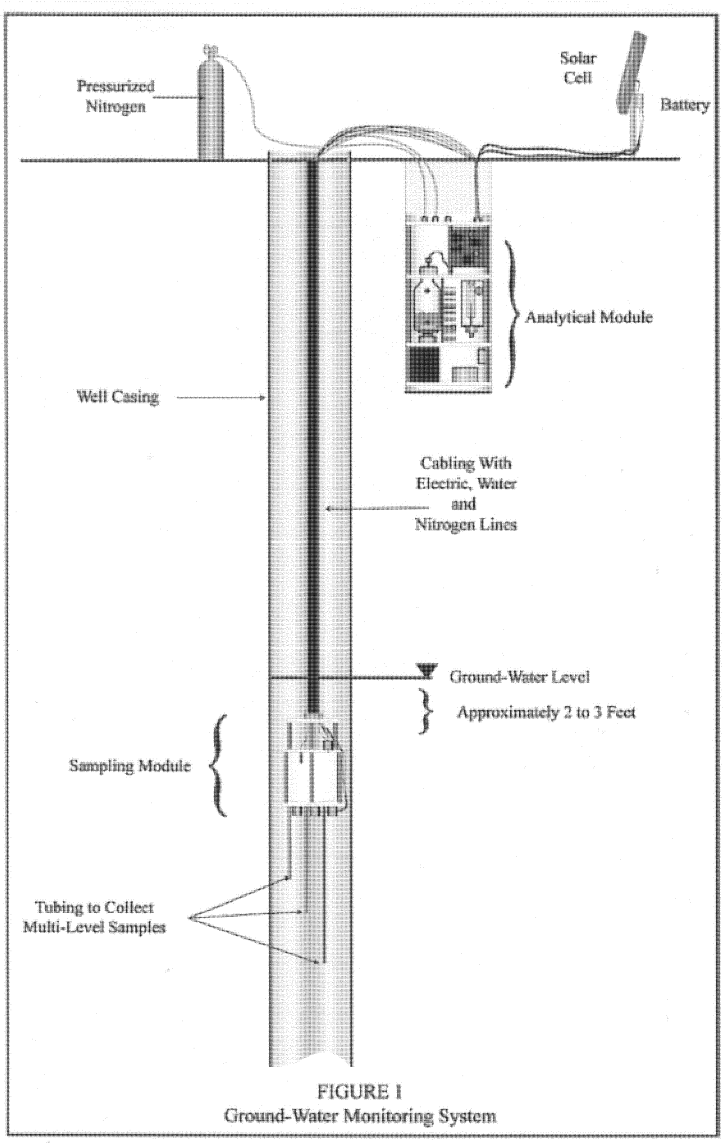


FIGURE 1
Ground-Water Monitoring System

through a tube located at the bottom of the sampling chamber to tubing which transfers the water sample to the surface. Because small volumes (150 to 200 mL) of the water is being transferred, the pressure to transfer the water sample is very low even for lifts of 100 feet.

Burge Environmental was invited to participate in the ETV program performed at the Stennis NASA Facility located in Alabama in August 1999. Burge Environmental tested a multi-level sampler monitoring four levels within a monitoring well. The actual tests were performed in a 92-foot high standpipe. The sample points tested by Burge Environmental were SP3, SP1O, SP12 and SP14 at depths of 90, 53, 35 and 16.5 feet respectively. The experiment included filling the standpipe with water containing a mixture of organic compounds (1,1-dichloro-ethene, 1,2-dichloroethane, benzene, trichloroethene, 1,1,2-tri-chloroethane and tetrachloroethene). The Burge Environ- mental sampler was configured to monitor the four sampling depths within the standpipe.

for multi-level sampling in existing wells. The sampling module was designed to allow for several modes of operation. The modes of operation include: 1) mounting of sensors directly in the monitoring well, 2) sampling and transport of water samples to the surface to sampling jars, or sensors, 3) purging of the ground water with nitrogen and transporting the volatile hydrocarbons to the surface in a stream of nitrogen. The mode of operation is based on the needs of the particular sensor being employed.

The module is illustrated in Figure 2. The module is composed of a sampling chamber which is located approximately 3 to 5 feet below the static water level of the ground water. There are several valves located under the chamber to select the depth of the water to be sampled within the monitoring well. Tubing is attached to each valve to the depth to be sampled. The sampling procedure is initiated by opening a valve to the selected depth and opening a second valve (at the top of the sampling chamber) which vents the sampling chamber to the atmosphere. The sampling chamber is filled with ground water based on the pressure differential. The sampling chamber continues to fill until the water contacts a water level sensor located near the top of the sampling chamber. The activation of the sensor causes the bottom sampling valve and the vent valve to close, and opens a valve which pressurizes the chamber (10 to 15 psi). The water in the chamber is conducted

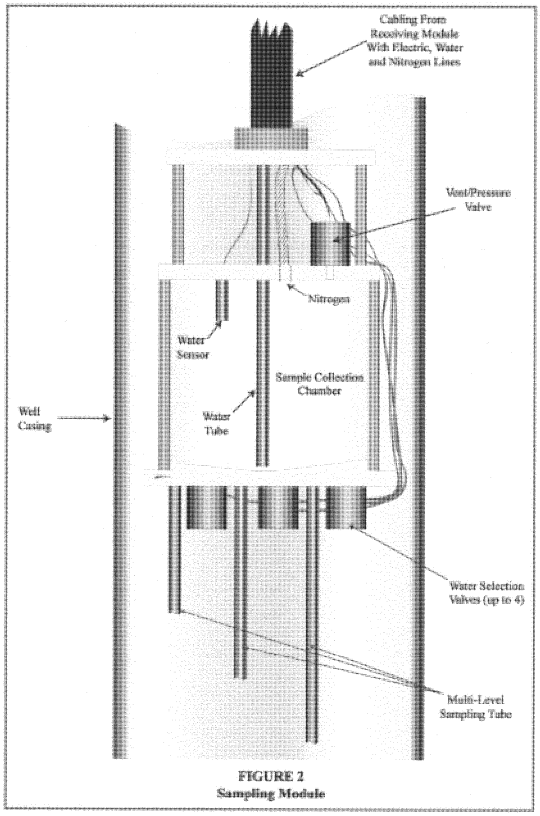


FIGURE 2
Sampling Module

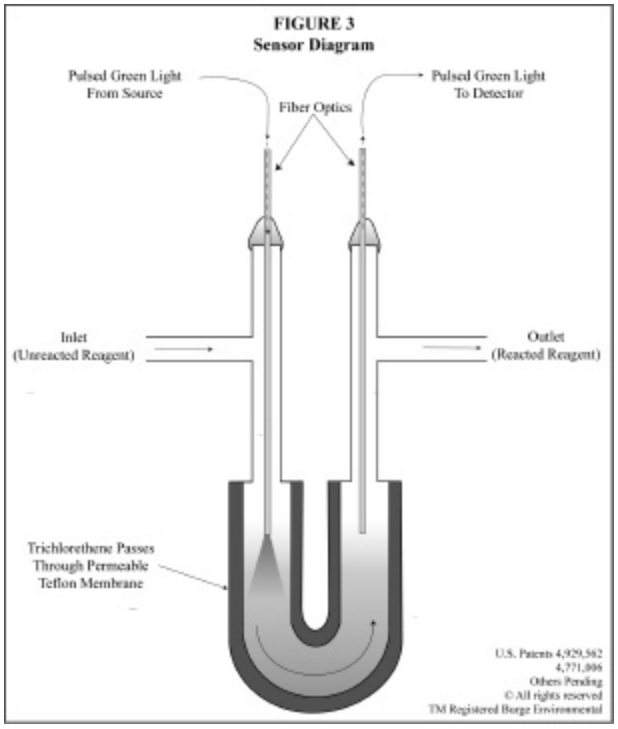
Experiment 1
The sampler was to collect five replicate samples at each depth. Simultaneously five samples (reference samples) were collected at each depth using the small taps located on the side of the standpipe. The samples were analyzed using a purge and trap sampler interfaced into a gas chromatograph/mass spectrograph. The control pump was a turbine pump placed into the standpipe and used to sample the water after the Burge Environmental sampler was removed.

Experiment 2
The standpipe was drained and filled with water containing a high concentration (150 to 200 ppb) of the same six organic compounds. This procedure was repeated for the collection of five samples from each sampling level for both the reference and Burge sampler.

Experiment 3
The final experiment was to drain the standpipe and fill it with water (blank) containing no detectable concentrations of the organic compounds. This experiment was used to assess the ability to collect five blank samples after collecting a high concentration of the organic compounds. A compilation of the results for TCE is presented in Table 1.

Table 1. ETV Results for Trichloroethene Burge Sampler, Reference and Control Pump TCE Concentration and %RSD

Level Name	Level Depth, ft	Burge µg/L %RSD	Reference µg/L %RSD	Control Pump µg/L %RSD
Experiment 1				
Low Conc/Deep	SP3 90 Feet	9.9 6.6	10.5 11.1	10.3/ 12.1
Low Conc/Mid Deep	SP10 53 Feet	13.2 10.6	15.4 14	
Low Conc/Mid Shallow	SP 12 35 Feet	12.1 15.5	15.9 16.1	
Low Conc/Shallow	SP14 16.5 Feet	12.3 5.8	14.7 11.1	12.6 10.5
Experiment 2				
High Conc/Deep	SP3 90 Feet	179.8 17.2	189.9 8.2	188 6.4
High Conc/Mid Deep	SP10 53 Feet	170.6 9.6	173 6.4	
High Conc/Mid Shallow	SP 12 35 Feet	148.8 5.4	195.6 2.0	
High Conc/Shallow	SP14 16.5 Feet	166.4 5.5	171.6 6.6	191.6 9.6
Experiment 3				
Blank/Deep	Non Detect	Non Detect	Non Detect	



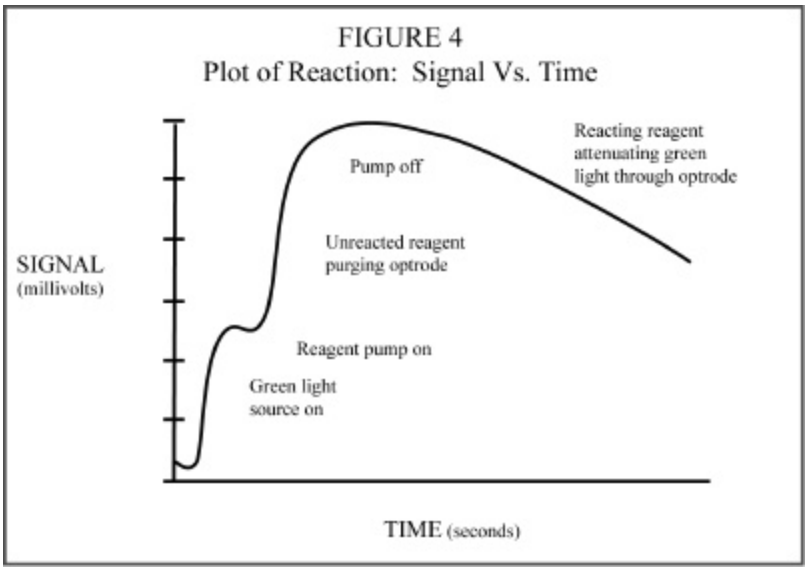
The results of the experiments indicated that transferring water was acceptable for 1,1-dichloroethene, 1,2-dichloroethane, benzene, trichloroethene and 1,1,2-trichloroethane. The experiments indicated the sampling system was not acceptable for tetrachloroethene (probably because of the Henry's Law Constant for this compound). This compound could be purged by the sampling unit instead of transferring as a water sample.

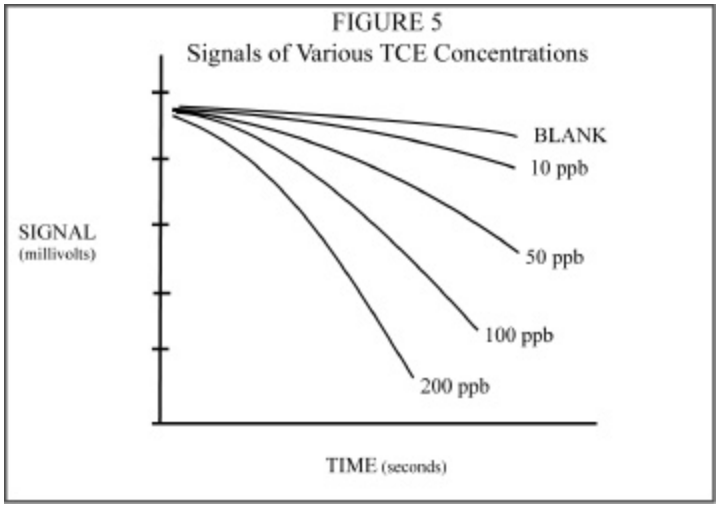
Sensor Module

The principle of detection is a quantitative, irreversible chemical reaction that forms visible light-absorbing products. The reaction is based on the Fujiwara reaction which has been used for many years for the detection of chlorinated hydrocarbons. The operational basis of the optrode is the measurement of the time history of the development of a colored product formed by the reaction of target compounds, TCE and chloroform, with specific reagents. The rate of change in color is directly proportional to the concentrations of target compounds to which the optrode is exposed.

A simplified illustration of the optrode is shown on Figure 3.

The operation of the optrode requires the reagent to be introduced into a permeable fluorocarbon tube. In the presence of the selected target compound, the reagent begins to react and there is a respective color (clear to red) change of the reagent. The pulsed green light passing through the sensor is attenuated by the resulting reagent reaction. The attenuation of the light is plotted versus the time of the reaction (Figure 4). The attenuation of the signal versus time over which the signal is measured is used to calculate a slope for a given TCE concentration. The slopes (rate of reaction) of several TCE concentrations, plotted versus time, are used to construct an analytical curve (Figure 5). The slope of the reaction of an unknown TCE concentration is compared against the slopes of standards to calculate the TCE concentration of the unknown.





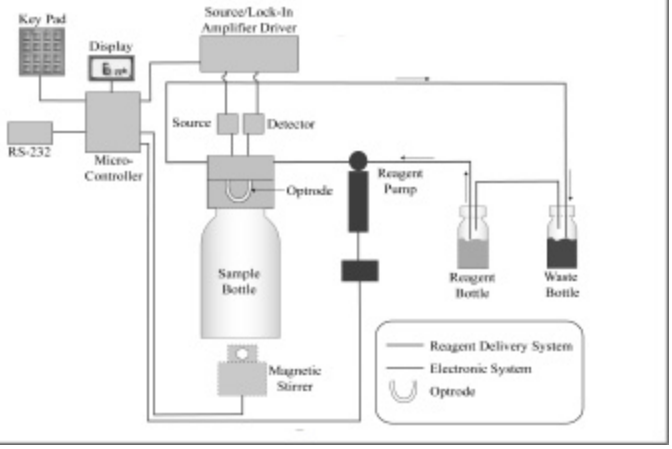
It requires approximately 3 to 4 minutes to perform an analysis, after an equilibrium concentration of TCE is presented to the sensor. Because the sensor cannot directly determine the TCE concentration in water, the sensor must be exposed to the head space above the water. It may require from 10 to 20 minutes for water containing TCE to equilibrate with the head space above the water. The limit of detection for TCE in ground water is 1 to 4 ppb with a linear dynamic range of 5 to 100 ppb. The specificity of the sensor for TCE and other commonly occurring chlorinated hydrocarbons is documented in Table 2.

Table 2. Selectivity of the Sensor for Volatile Chlorinated Hydrocarbons Commonly Occurring in Ground Water Systems

Compound	Reaction for 100 ppb Solution	100 ppb solution of the Compound gives the same Signal as X ppb of TCE
1,1,1-Trichloroethane	None	Same as Blank
Tetrachloroethene	None	Same as Blank
Methylene Chloride	None	Same as Blank
Trans-1,2-Dichloroethene	None	Same as Blank
Cis-1,2-Dichloroethene	None	Same as Blank
1,1-Dichloroethene	None	Same as Blank
Chloroform	Slight	Same as 15 ppb
Vinyl Chloride	None	Same as Blank
Carbon Tetrachloride	None	Same as Blank

The design of the sensor module is illustrated in Figure 6. The design includes a syringe pumping system for delivering the reagent to the sensor, optical/electronics system for providing a signal (pulsed green LED) and receiving the signal after passing through the reagent in the permeable tube.

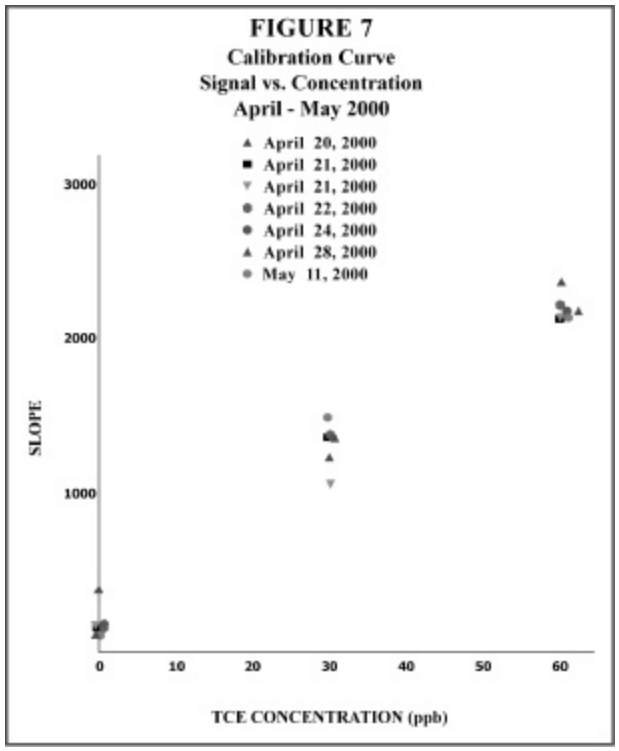
FIGURE 6
Instrument Schematic



Calibration System

The calibration system injects (with either a syringe pump or a sampling loop) a known volume and concentration of standard into the sample bottle. The system is capable of presenting the sensor with a blank and one to four concentrations of TCE. The most commonly used standard injected is sufficient to create a 30 ppb TCE concentration in the 500 mL of water used during an analysis. A 60 ppb is created by injecting twice the amount of standard into the sample bottle. A graph of the calibration of the sensor for several days using a blank, 30 ppb and 60 ppb standard is illustrated on Figure 7.

FIGURE 7
Calibration Curve
Signal vs. Concentration
April - May 2000



Support and Control /Data Handling Module

The support modules include the delivery of compressed air (air tank) and power (solar cell) to the monitoring system. The data handling system includes the control of the modules, data acquisition and calculations.

Future Work to be Reported at Conference

It is anticipated that field trials will be performed at Homestead Air Force Base, Florida, in July and August 2000. The preliminary results of the field trials will be presented at the conference.

A NOVEL SENSOR SYSTEM FOR MEASURING VOCS IN AIR AND WATER

Peter Lo
American Research Corporation of Virginia, P.O. Box 3406, Radford, VA 24143

A novel integrated sensor system that accurately and rapidly measures small quantities of volatile organic compounds (VOCs) both in air and in aqueous environments is presented. The sensor combines sensitive diode laser-excited fluorescence with total internal reflection methods of analysis to provide a real-time, continuous monitor of VOCs. A description of the sensor platform is presented. Experimental results in demonstrating the sensor platform for use with several highly sensitive polymer/dye films in detection of aqueous and gaseous phase VOCs are described. The detection for both aqueous and vapor phase trichloroethylene using fluorescence spectroscopy is in the part-per-billion to 100 part-per-million range. This sensor platform is significant in providing real-time identification and quantification of volatile organic compounds and environmental pollutants in groundwater, soil, effluent discharge and fugitive emissions.

IMPLEMENTATION OF IMPROVED PROTOCOLS FOR SAMPLING AND ANALYSIS OF VOLATILE ORGANICS IN SOILS

Frank R. Allen, Chemist and Diane Guthrie, P.E.
USEPA Region 4, 980 College Station Rd., Athens, GA 30605

SW 846 Method 5035 was promulgated in June 1997 to describe collection and preparation of soils and oily wastes. High level samples (defined as having concentrations above 200 µg/kg) were included, but their sampling and analysis was unchanged. However, the sampling and analytical requirements for low level samples (defined as under 200 µg/kg) were improved to reduce loss of volatile organic compounds by volatilization and/or biodegradation. The data quality and sampling objectives of each project should be evaluated to determine the applicability of the high or low level procedures due to the differing detection limits which may be obtained and the increased handling of each sample. This new method is superior and more sophisticated requiring increased coordination between field and laboratory personnel. Additional laboratory or field equipment may be required before using Method 5035.

There are four preservation options available for low level sampling, each having advantages and disadvantages. The first option is the use of the Encore™ sampler which is user-friendly but requires 2 to 3 samplers per location. Limited sample volume reduces the representativeness of the samples, possibly increasing the number of locations. Samples taken with the Encore™ must be preserved within 48 hours. This time limitation may overwhelm the laboratory staff with a large number of sample preparations. The second preservation option is acidification in the field with sodium bisulfate in a pre-prepared 40-ml vial. This option has the advantage of immediate preservation of the sample and a 14-day holding time. However, sodium bisulfate is a strong acid which may react with samples, particularly calcareous soils; shipments using this preservative are limited by hazardous material regulations. A third preservation option is storage at -10ºC. Temperature preservation has been used successfully in calcareous areas of Region 4 or where field logistics limit return of unpreserved samples to the laboratory. The sample is placed in a pre-prepared vial containing reagent water and frozen laterally to reduce breakage and to keep pressure on the cap liner to verify the seal. The vial is brought to room temperature before analysis. Since freezing retards biodegradation, the standard 14-day holding time is deemed applicable by Region 4. The last preservation option is methanol. Although this procedure has been used by laboratories, there are several items which must be considered for field applications: methanol is a hazardous material and should be handled and shipped appropriately; when used under field conditions, it may absorb ambient contaminants; the vials require extensive preparation before and during use; higher detection limits are associated with this option, but the extracts may be composited yielding a more representative sample than the other options.

THE EFFECTS OF TEMPERATURE, SAMPLE CONTAINER, AND PRESERVATIVE ON VOLATILE ORGANIC COMPOUNDS IN SOIL

Mike Zimmerman, Analytical Group Leader and Keith Strout, Senior Organic Chemist
IT Corporation, Quality Assurance Technical Support Laboratory (QATS),
2700 Chandler Avenue, Building C, Las Vegas, NV 89120
Eric S. Reynolds and Terry Smith
U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Analytical Operations Center, 401 M Street S.W., Washington, DC 20460

ABSTRACT

The sampling and analysis for volatile organic compounds (VOCs) in soil are the subject of continuing research and development by the U.S. Environmental Protection Agency (USEPA) and other agencies. This paper describes single laboratory experiments designed to evaluate the differences in several types of soil samples using three (3) soil types spiked in the laboratory with VOCs and analyzed at three (3) holding times (1, 7, and 14 days). A larger multi-laboratory study is underway which includes frozen EnCores® and SW-846 Contract Laboratory Program (CLP) Method 5035 sodium bisulfate-preserved samples. Results of more single-laboratory analyses, including frozen EnCores® and sodium bisulfate-preserved samples, and the multi-laboratory study results will be presented as they become available. The sample types reported here are listed below:

1 - Frozen Closed-System 40 mL Containerized Samples - no preservative
2 - Closed-System Samples with water stored at 4ºC
3 - Closed-System Samples with 4% methanol preservative stored at 4ºC

The results of theses analyses indicate that frozen storage without water or methanol yields the most consistent results. Styrene losses and acetone formation were not observed in the frozen samples. Although some losses of the most volatile target compounds were seen in the frozen samples, recoveries of the CLP target compounds range from approximately 30% to 90% over 14 days of frozen storage.

INTRODUCTION

Closed-system purge-and-trap analysis for low concentration VOCs in soil is a significant improvement on the bulk sampling and laboratory sub-sampling methods of the past. The use of EnCore and other sampling devices have also provided more accurate analysis for VOCs in soil. Refrigeration and the use of sodium bisulfate preservation, however, may not be the best choices for storage and preservation. The use of sodium bisulfate as a preservative in closed-system purge-and-trap soil VOC analysis is known to degrade styrene and may contribute to the formation of acetone[1,2]. Sodium bisulfate also effervesces in alkaline and carbonaceous soils and precipitates in the purge-and-trap systems. Frozen storage has been used in many EPA and other agency projects and is examined here as an alternative to chemical preservation. As alternative preservatives, water with no additives and four percent (4%) methanol are examined. Four percent methanol is the maximum amount of methanol in water recommended by EPA for purge-and-trap analysis[3,4]. Methanol preservation and extraction for analysis of VOCs in soil has been evaluated in previous studies but is omitted here because it is limited to concentrations greater than approximately 200 µg/Kg.

SOIL TYPES

Three (3) soil types identified as Virginia A, Virginia B, and INEEL were used in this study. These soils are well-characterized and representative of three general soil types. The Virginia soils are from the USEPA EMAP program and were provided by the USEPA-Las Vegas National Exposure Research Laboratory (NERL). The INEEL soil is from the U.S. Department of Energy Idaho National Engineering and Environmental Laboratory and has been used by EPA for several years at QATS in the preparation of performance evaluation samples (PESs). Table 1 lists the percent sand, silt, clay, and total carbon for the three soils. Virginia A is a high organic, black, sandy soil. Virginia B is a high clay, silty, orange soil. INEEL is a high sand, gray soil.

SPIKING, STORAGE, AND ANALYSIS

The spiking was performed at the QATS Laboratory using methanol:water solutions of the target compounds to achieve soil concentrations of 20 µg/kg and 160 µg/kg, including all forty-eight (48) current CLP target VOCs. All of the soil samples were brought to 5% moisture prior to spiking by addition and mixing with laboratory water. Duplicates samples were spiked and analyzed at two concentrations, 20 µg/Kg and 160 µg/Kg, for each soil type at each holding time. All of the samples were analyzed at the QATS Laboratory using the current CLP OLM04.2 modified SW-846 Method 5035 heated purge-and-trap GC/MS procedures. The frozen samples were analyzed by

adding 5 mL of laboratory water at the time of analysis. CLP system monitoring compound (SMC) recoveries ranged from 76.8% to 119% in the frozen and water-preserved samples. Bromofluorobenzene recovery in the 4% methanol-preserved soils was very low, decreasing with each day's analyses to values near 6%.

Table 1. Virginia A, Virginia B, and INEEL Soil EMAP-Forests Accuracy Windows for Virginia A and Virginia B Soils, Units: Percent (%)

Parameter	Virginia A		Virginia B		INEEL	
	Low	High	Low	High	Low	High
Sand	60.08	69.27	12.66	19.91	85	95
Silt	23.93	31.90	46.46	53.52	1	5
Clay	5.90	9.06	31.46	35.97	1	5
Total Carbon	1.74	3.39	0.60	0.84	0.1	1

RESULTS AND DISCUSSION

Recoveries for twelve of the target compounds spiked at 160 µg/Kg in Virginia A soil are listed in Tables 2 through 4. S1 and S2 are designations for duplicate samples number one and two, respectively. In Table 5, the recoveries and relative standard deviation (RSD) for all of the samples for each soil type stored frozen are summarized.

Table 2. Recovery (%) from Virginia A Soil Frozen at -12ºC in 40 mL Closed System Containers, No Preservative

Target Compounds	Day 1		Day 7		Day 14		All Samples	
	S1	S2	S1	S2	S1	S2	Ave	RSD
Dichlorodifluoromethane	61.5	74.5	53.2	42.5	27.0	41.8	50.1	33.3
Vinyl chloride	72.5	90.2	56.9	44.5	32.7	53.1	58.3	35.1
1,1-Dichloroethene	76.0	89.7	67.2	63.2	53.5	63.4	68.8	18.2
Acetone	66.5	130.0	53.1	48.9	89.0	88.6	79.4	37.9
Methyl t-butyl ether	80.1	94.0	81.7	81.4	78.3	80.9	82.7	6.8
Benzene	81.7	99.0	76.3	76.9	69.4	70.2	78.9	13.8
Trichloroethene	70.5	82.1	68.7	68.3	63.6	65.2	69.7	9.4
Toluene	84.5	103.0	76.5	78.3	75.2	72.8	81.7	13.6
Tetrachloroethene	68.9	77.3	65.9	66.9	63.9	63.1	67.7	7.6
Styrene	62.8	72.0	63.2	63.8	62.1	59.1	63.8	6.8
1,2-Dibromoethane	65.4	78.7	61.9	63.8	64.6	66.3	66.8	9.0
1,2,4-Trichlorobenzene	32.8	52.7	29.9	30.9	36.4	35.1	36.3	23.1

The losses of styrene and high values for acetone previously reported in sodium bisulfate-preserved samples were not seen in the samples frozen without preservative. Recoveries from the frozen samples range from approximately 36% for 1,2,4-trichlorobenzene to 83% for MTBE. In these samples, approximately ten to twenty percent of the dichlorodifluoromethane and vinyl chloride was lost with each week of storage. Acetone results are the most variable but does not appear to have been formed in these samples.

Table 3. Recovery (%) from Virginia A Soil Water Preservation Stored at 4ºC

Target Compounds	Day 1		Day 7		Day 14		All Samples	
	S1	S2	S1	S2	S1	S2	Ave	RSD
Dichlorodifluoromethane	55.2	52.0	48.2	27.1	43.4	43.4	44.9	22.0
Vinyl chloride	87.2	80.0	83.4	50.8	69.0	68.5	73.2	18.2
1,1-Dichloroethene	78.3	74.0	73.0	57.2	64.2	66.6	68.9	11.2
Acetone	78.7	68.0	89.4	72.9	60.9	52.4	70.4	18.6
Methyl t-butyl ether	121.0	121.0	88.2	89.1	83.3	84.4	97.8	18.5
Benzene	75.5	73.1	69.7	71.8	63.4	65.3	69.8	6.7
Trichloroethene	66.4	63.8	61.5	58.1	51.8	56.0	59.6	9.0
Toluene	78.8	76.1	71.2	74.0	65.0	64.5	71.6	8.2
Tetrachloroethene	68.4	68.4	64.8	61.2	58.1	58.8	63.3	7.3
Styrene	61.6	56.6	36.8	49.4	39.0	4.9	41.4	49.1
1,2-Dibromoethane	68.5	66.6	60.4	59.5	48.1	54.1	59.5	12.8
1,2,4-Trichlorobenzene	22.6	20.5	20.9	21.7	18.0	17.8	20.3	9.6

Table 4. Recovery (%) from Virginia A Soil 4% Methanol Preservation Stored at 4ºC

Target Compounds	Day 1		Day 7		Day 14		All Samples	
	S1	S2	S1	S2	S1	S2	Ave	RSD
Dichlorodifluoromethane	48.9	53.8	42.3	43.1	43.6	45.3	46.2	9.6
Vinyl chloride	84.3	98.2	73.5	77.3	66.3	71.5	78.5	14.5
1,1-Dichloroethene	27.5	30.2	24.0	24.7	20.7	22.2	24.9	14.0
Acetone	56.3	45.9	70.6	59.4	42.4	39.9	52.4	22.5
Methyl t-butyl ether	80.1	84.5	84.0	79.4	62.2	60.9	75.2	14.3
Benzene	73.0	76.3	72.1	76.5	67.3	66.1	71.9	6.1
Trichloroethene	68.2	72.3	61.6	61.9	77.9	83.8	71.0	12.5
Toluene	75.3	79.0	89.4	98.4	76.2	85.9	84.0	10.7
Tetrachloroethene	76.8	104.0	76.9	89.1	103.0	107.0	92.8	14.9
Styrene	56.0	55.4	18.4	17.4	13.2	12.4	28.8	72.8
1,2-Dibromoethane	75.1	76.7	72.7	73.3	64.1	71.1	72.2	6.1
1,2,4-Trichlorobenzene	0	0	0	0	0	0	0	na

Styrene losses in the water-preserved samples are similar to the losses previously reported using sodium bisulfate. Losses of dichlorodifluoromethane and vinyl chloride over the two weeks of storage are slightly less than the losses in the frozen samples.

Problems with the 4% methanol preserved samples include low recovery of 1,1-dichloroethene, styrene losses with time similar to the water and sodium bisulfate preserved samples, and zero recovery for 1,2,4-trichlorobenzene. Low recoveries were noted for many of the other target compounds not listed here, including the dichlorobenzenes, 1,2-dibromo-3-chloropropropane, bromoform, and 1,1,2,2-tetrachloroethane. The losses are thought to be related to the large amount of methanol purged onto the VOCARB 4000 trap. On each day of analysis, the response for these compounds decreased with each run suggesting an accumulation of methanol. Bromofluorobenzene (BFB) low recoveries were mentioned earlier. Since BFB is an SMC added immediately prior to analysis, its low recovery further supports the conclusion that low recoveries in the 4% methanol samples is an analytical problem unrelated to sample storage or soil absorption. Efforts to accommodate the methanol have been unsuccessful using the VOCARB trap. Analyses with a tenax/silica gel/charcoal trap are underway.

Table 5. Recovery (%) and RSD from Three Soil Types over 14 Days Frozen Storage at -12°C Without Preservatives

Target Compounds	Virginia A			Virginia B			INEEL		
	Ave %Rec	RSD	n	Ave %Rec	RSD	n	Ave %Rec	RSD	n
Dichlorodifluoromethane	52.2	35.2	12	59.0	16.0	12	57.8	28.4	12
Vinyl chloride	59.8	37	12	70.5	21.0	12	64.1	33.1	12
1,1-Dichloroethene	75.8	23.9	12	77.8	15.9	12	75.8	33.1	12
Acetone	86.1	32.6	12	cont.			112	78.7	12
Methyl t-butyl ether	91.0	13.8	12	87.4	15.2	12	84.6	15.8	12
Benzene	84.0	12.7	12	85.2	9.4	12	74.4	24.6	12
Trichloroethene	89.7	25.9	12	85.6	26.0	12	84.1	44.5	12
Toluene	92.9	15.9	12	88.6	15.3	12	75.9	27.6	12
Tetrachloroethene	103.0	37.5	12	84.7	35.8	12	78.5	47.4	12
Styrene	76.3	17.8	12	80.0	21.4	12	78.3	30.6	12
1,2-Dibromoethane	85.4	25.7	12	95.2	29.4	12	79.5	34.2	12
1,2,4-Trichlorobenzene	37.8	16.5	12	68.8	38.2	12	77.2	34.5	12

Table 5 is a summary of the results from the 5-gram spiked samples frozen in 40 mL purge-and-trap vials and analyzed at the three holding times. Duplicate high and low concentration samples were spiked and analyzed to total 12 samples for each soil type. The containers contained stir-bars and were analyzed without exposure. In all cases, the results indicate good recovery and reasonable precision for VOCs in soil. Virginia B soil is contaminated with acetone at approximately 5 ppm. With the exception of the relatively low recovery of 1,2,4-trichlorobenzene in Virginia A soil, the differences in VOC recovery and precision between soil types were negligible.

SUMMARY

Frozen storage without preservation provided the most accurate and precise results for the most number of target compounds in these analyses. Water preservation led to losses of styrene. Recovery for many of the heavier target compounds is low or zero with 4% methanol.

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STUDY OF ACETONE PRODUCTION IN SW-846 METHOD 5035 (LOW LEVEL) ASSOCIATED WITH VARIOUS PRESERVATION TECHNIQUES AND STORAGE CONDITIONS

M. Uhlfelder
Severn Trent Laboratories, Inc., 19 Loveton Circle, Sparks, MD 21152

The low-level procedure of the U.S. EPA SW-846 Method 5035 (Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples), specifies that soil samples be preserved to a pH < 2 in a closed-system container using an aqueous sodium bisulfate solution (0.2 grams per 1.0 gram of sample). This preservation can be done in the field, or in the laboratory within 48 hours of sampling if collected and transported in a closed-system sampling device (i.e., EnCore sampler) at 4 ° C + 2 ° C. After preservation, the sample is stored at 4 ° C + 2 ° C in the closed-system container until analysis. However, under these preservation and storage conditions, it has been found that degradation of certain commonly determined analytes (e.g., styrene), and the formation of acetone, may occur. Several preservation and storage techniques for most of the commonly determined Volatile Organic Compounds (VOCs), where evaluated over time, using a characterized soil sample. These techniques included: 1) spiked samples stored at 4 ° C + 2 ° C after preservation with sodium bisulfate in a closed-system container (method specified technique); 2) spiked samples stored frozen at -12 ° C + 3 ° C after preservation with sodium bisulfate in a closed-system container; 3) spiked samples stored at 4 ° C + 2 ° C after being prepared in DI water in a closed-system container; 4) spiked samples stored frozen at -12 ° C + 3 ° C after being prepared in DI water in a closed-system container; 5) spiked samples stored at 4 ° C + 2 ° C in the EnCore samplers; and 6) spiked samples stored at -12 ° C + 3 ° C in the EnCore samplers. The tests covered a 14 day time period, which represents the method specified maximum holding time for Volatile analyses in a soil matrix. Replicate spiked samples from each preservation and storage technique were analyzed initially (Day 0) and every other day throughout the test period (Days 2, 4, 6, 8, 10, 12 and 14). The results and recommendations from these evaluations are presented.

LARGE VOLUME INJECTIONS

R. McMillin

No abstract available.

INNOVATIONS IN LARGE VOLUME INJECTION:
APPLICATIONS OF A CHROMATOGRAPHIC ZONE AS AN INLET SYSTEM FOR GC/MS

Dennis R. Gere and Harry Prest
Agilent Technologies, Palo Alto, CA and Wilmington, DE
Greg O'Neil, Jeff Hollis and Rick Herrman
Apex Technology, Cincinnati, OH

In this talk, we will present a new, innovative approach to the injection of liquid samples. In typical GC/MS analyses, only a fraction of the injected components is of analytical interest; the remainders are interferences or uninteresting (e.g., sample solvent). Eliminating these unnecessary components provides substantial improvements such as increased analytical integrity, less frequent maintenance, and so forth.

These concerns become amplified in Large Volume Injection (LVI). A recent advance in injection port technology, the Apex ProSep, provides several approaches to selecting which components are introduced onto the GC column. This talk presents a demonstration of selected ProSep capabilities and some environmental applications.

The ProSep system consist of 4 components: the pre-column module which is the inlet port, two control modules which control the flow and column temperature, and a glass or silica pre-column which fits inside the pre-column module similar to a split/splitless glass liner.

We will show an example of injecting PCB samples with an injection of 75 µl. We will show two of the most toxic of the PCB congeners – the non-ortho substituted penta and hexa – chlorinated biphenyls at 1 fg/µl. The chromatogram shows analysis using 2 ion ECNI SIM with large volume injection. There is very good signal with mass spectral confidence at a concentration typically attainable only with ECD. (This is about 1.2 million molecules per µl.)

Another example of the use of the large volume injection is the analysis of NDMA. (N-nitroso dimethyl amine) This is one of the analytes in Method 8270. NDMA is a suspected human carcinogen and teratogen present in nitrated-cured meats, cooked foods, tobacco smoke and unfortunately, beer. In the environment, NDMA has been found in the atmosphere of tire factories, tanneries, and metalworking, chemical and mining facilities. NDMA is also associated with rocket fuel both as a contaminant and a degradation product. Based on risk assessments NDMA has been regulated in drinking water sources at the 0.7 ng/L (ppt) level by the US-EPA and at 2 ng/L (ppt) by California Dept. of Health Services. However, existing methods have detection limits in the 7-100-ng/L range; 4 to 10 times higher than the regulated limits.

Primarily two extraction approaches exist for NDMA in water (liquid-liquid, solid-phase extraction) but a variety of detection schemes have been applied (NPD, chemiluminescent nitrogen, and high-resolution mass spectrometry). The electron impact (EI) mass spectra of NDMA yields ion fragments at m/z=74,42,43 as the major ions. Because the m/z= 43 and 42 AMU EI fragments are easily compromised by interferences, positive chemical ionization (PCI) offers a better approach. Typically a 1L water sample is extracted and concentrated 500 to 1000 fold into a solvent such as CH_2Cl_2. Unfortunately, extraction efficiencies are typically unfavorable. LVI has the potential to enhance NDMA detection limits

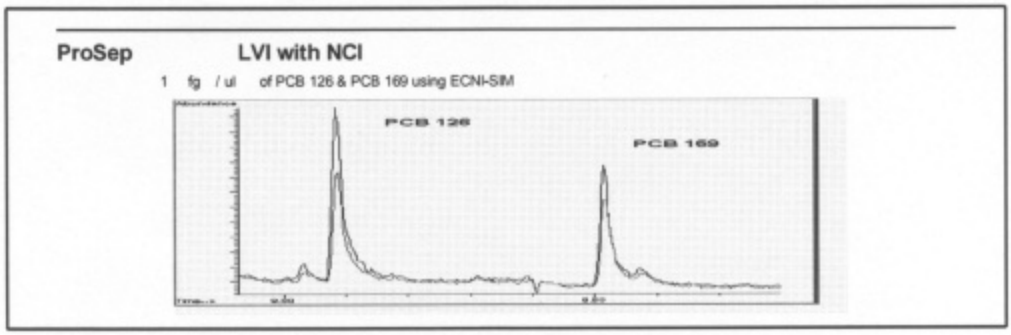


Figure 1. LVI of PCBs 1 femtogram per microliter

The data illustrates the capability of the Apex ProSep Pre-column Separation Inlet to make separations in LVI mode and behave as a chromatographic zone. If there were no separating power, selectively removing components would

not be possible. It must be emphasized that in this mode of operating the ProSep, it does **not** behave as a programmed thermal vaporization (PTV) or desorption inlet although it can be made to function as such. Other techniques of selectively introducing compounds onto the analytical column are also available via ProSep. Work with authentic samples and a wide variety of matrices has shown the ProSep to be very reproducible and robust. Injection is rapid so sample throughput is very high.

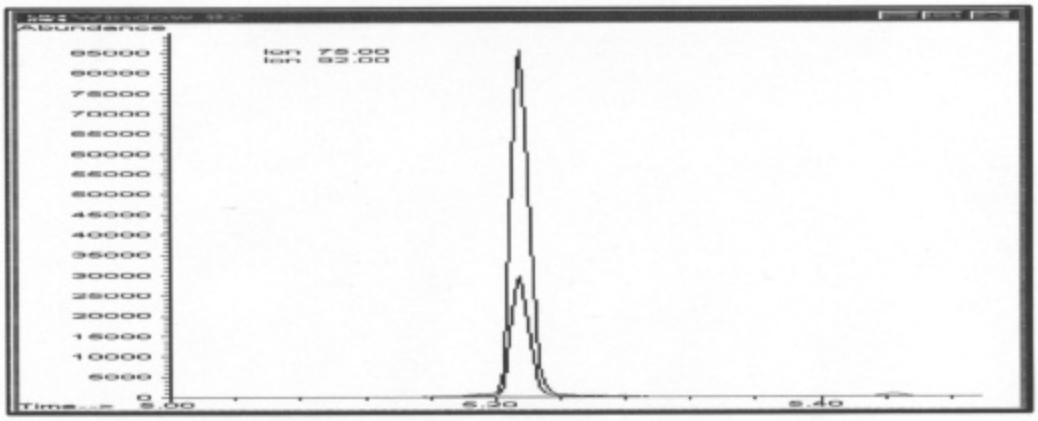


Figure 2. LVI of N-nitroso dimethyl amine at 200 ppt

AUTOMATED EXTRACTION OF LARGE SAMPLES FOR ENVIRONMENTAL ANALYSIS USING ACCELERATED SOLVENT EXTRACTION (ASE)

Bruce Richter
Dionex, SLCTC, 1515 W. 2200 S., Suite A, Salt Lake City, UT 84119

The development and use of automated extraction technology for the environmental laboratory has enabled analysts to dramatically reduce the amount of organic solvents used and the amount of time required in the sample preparation process. These systems generally use sample sizes smaller than those used in Soxhlet or sonication extraction. In many cases, this is acceptable, but there are situations where larger samples must be used in order to achieve the desired detection limits. For example, it is common to use 30-g samples for the analysis of semivolatile compounds. If the samples are wet and require the addition of a desiccant such as sodium sulfate, the volume of the sample will be too large for the available extraction cells.

The use of accelerated solvent extraction (ASE) has grown rapidly since its introduction nearly 6 years ago. ASE complies with the requirements of Method 3545A for the extraction of organochlorine pesticides (OCPs), semivolatile compounds (BNAs), chlorinated herbicides, polychlorinated biphenyls (PCBs), organophosphorus pesticides (OPP), polychlorinated dibenzo-p-dioxins and furans, diesel range organics (DROs) and waste oil organics (WOOs). The advantages of ASE include short extraction times (generally less than 15 min) and small solvent quantities used (generally less than 50 mL) for extracting solid and semisolid samples. Until now, the largest sample capacity cell for use in ASE has been 33 mL. By scaling up the necessary components of the technology, sample cells are now available in 34-, 66- and 100-mL sizes. This allows the use of ASE for applications previously difficult to perform. Data will be shown using this approach for the extraction of BNAs and WOOs from soil samples, PCBs from fish tissue, and OPPs from fruits and vegetables. In all cases, the sample sizes will be 30 g or larger. The bias, precision and method detection limit values will be reported for these samples.

Automated extraction instrumentation with this capability will greatly increase the productivity of environmental laboratories while saving time and expenses and increasing safety by decreasing solvent exposure.

ANALYTICAL METHOD DEVELOPMENTS TO SUPPORT PARTITIONING INTERWELL TRACER TESTING

Mark L. Bruce, Technical Advisor, Raymond M. Risden, GC Group Leader and Jeffery Smith, Project Manager
Severn Trent Laboratories, 4101 Shuffle Dr., North Canton, OH 44720
(mbruce@stl-inc.com)
Randy Parker
U.S. Environmental Protection Agency, National Risk Management Research Laboratory,
Office of Research and Development, Superfund Innovative Technology Evaluation Program,
Cincinnati, OH 45268
William Kosco, Dr. John Thompson and Dr. Greg Swanson
Tetra Tech EM Inc., 250 West Court Street; Suite 200W, Cincinnati, OH 45202
Allan M. Tordini
Quality Works, Inc., 8 Strafford Circle Road, Medford, NJ 08055

Abstract
The modified Method 5031 successfully separates the tracer alcohol analytes from potential interferences associated with acid preservatives, dissolved salts and surfactants. Recovery of tracer alcohols is generally in the 80-110% range. Azeotropic distillation (Method 5031) can be extended to the high-boiling tracer alcohols to allow tracer analysis at concentrations down to 0.1 ppm. The holding time study is underway and demonstrates analyte stability for at least one week for both acid preserved and unpreserved samples.

Introduction
The partitioning interwell tracer test (PITT), was developed during the early 1990s by Dr. Gary A. Pope of the University of Texas. The test is used to perform *in situ* measurement of non-aqueous phase liquid (NAPL) in an aquifer. The PITT is based on injection of a mixture of tracer compounds (typically alcohols) with varying affinities for the NAPL in one or more wells in a well field, and extraction of the tracers from other wells in the field. Tracers with low or no affinity for the NAPL (low partition coefficient) will pass through the study zone more quickly than those with a higher affinity for the NAPL (higher partition coefficient). By studying the rate at which each tracer moves through the study zone, knowing the estimated partition coefficient of each tracer, the amount of NAPL present in the zone can be calculated. In essence, a PITT is a chromatographic separation of a mixture of tracers. For a saturated-zone PITT, water is the mobile phase. Tracer alcohols are the analytes and the NAPL in the ground is the “chromatographic stationary phase”.

The main advantage of a PITT is the ability to estimate NAPL quantity over a large spatial volume with minimal site drilling as opposed to traditional soil core sampling. Therefore PITTs can be used to measure the overall contaminant removal efficiency of a treatment process. By performing PITTs both before and after treatment of a contaminated aquifer, the amount of contaminant removed can be determined.

Historically the tracer alcohol analysis has been performed by gas chromatography with flame ionization detection (GC-FID) with direct aqueous injection (DAI). Unfortunately the lack of a sample cleanup and concentration steps may introduce other sample components that damage the chromatographic system, degrade performance and limit quantitation levels to about 1 mg/L. Specifically, some post-remediation PITT water samples are expected to contain both salts and surfactants. Sample cleanup by distillation has been used to separate volatile and semi-volatile analytes from less volatile interferences there-by improving gas chromatographic reliability. In addition, azeotropic distillation has been used to concentrate the analytes into a smaller volume, thus improving analytical sensitivity. This work extends SW-846 Method 5031 to sample cleanup without analyte concentration and to include alcohols with 6 to 8 carbon atoms that are commonly used as alcohol tracer compounds.

Historically direct aqueous injection samples have not been chemically preserved with inorganic acids to retard biological activity. Instead, refrigeration has been used to slow biological degradation. Thus, sample storage time has been limited and uncertain. The use of acid preservatives is common and effective for volatile organic analytes. Unfortunately, direct injection of the acid into a GC damages the column and degrades performance. If the acid is neutralized, then distillation can effectively remove the analytes from the remaining salt. A sample holding time study is in process to determine the effects of chemical preservation and length of refrigerated storage.

Experimental
The azeotropic distillation process is described in EPA SW-846 Method 5031. It has been modified for those samples with high analyte concentrations that require interference removal without analyte preconcentration. The modified Method 5031 process uses a LabCrest/Andrews Glassware ammonia distillation system. The modified method is performed as follows: 1) Transfer VOC vial (40 mL) of sample to boiling flask with boiling chip. 2) Add surrogate and matrix spike solutions as appropriate. Neutralize sulfuric acid preservative when present with sodium hydroxide. Add antifoam agent (up to 10 mL) when surfactants are present in sample. 3) Add 15 mL of deionized water to collection vial. Assemble boiling flask, condenser, drip tube and collection vial. Place boiling flask in heating block. 4) Boil sample until 20 mL of sample have distilled over and dilute to a final volume of 40 mL. 5) Analyze distillate by GC-FID (Method 8015).

The following tracer alcohols were included in this study: 1-propanol, 2-propanol, 2-butanol, 1-hexanol, 1-heptanol, 2-ethyl-1-hexanol and 1-octanol. Surrogate alcohols were hexafluoroisopropanol and isobutanol.

Modified Method 5031 (preliminary results)
Samples preserved with sulfuric acid have been successfully neutralized and very little (<5 ppm) sulfate is carried into the distillate. Small amounts of aerosol may transport dissolved sulfate through the condenser. Samples preserved with hydrochloric acid (HCl) or containing a chloride salt (e.g. calcium chloride) and preserved with sulfuric acid distill over small amounts of HCl, resulting in distillates with ~ 20 ppm chloride and pH of 3 to 4. This acid in the distillate is likely to cause cumulative damage to the chromatographic system. Neutralizing the sample prior to distillation prevents HCl from distilling over with the alcohol analytes.

Post-remediation PITT samples may contain calcium chloride levels above 2,000 ppm and surfactant levels of 500 ppm. As mentioned above neutralizing the acid preservative prior to distillation prevents interference from the calcium chloride salt. Addition of up to 10 mL of antifoam agent (Baker Antifoam B Silicone Emulsion) effectively prevents foaming in the distillation flask.

Both surrogate alcohols were recovered well when the pH of the distilled sample was about 7. However, when the pH of the sample after “neutralization” of the acid preservative was about 12, the recovery of hexafluoro-isopropanol dropped to the 10-20% range. Isobutanol recoveries remained high in the 80-110% range.

The higher molecular weight tracer alcohols have very limited water solubility, particularly 1-octanol. When distilling samples that are nearly saturated with this alcohol, it appears that the 1-octanol comes out of solution and coats the inside of the condenser drip tube, decreasing the efficiently with which it is transferred into the collection vial. These drops of nonpolar “solvent” apparently dissolve portions of the other high molecular weight alcohols. Thus, recoveries from the high concentration samples for these analytes is low (30-60% range) and less reproducible than low concentration samples. Dilution of the high concentration samples prior to distillation allows the analyst to avoid this solubility limitation.

Method 5031: Expanded Analyte List (preliminary results)
When Method 5031 was originally developed 10 years ago it was not expected to work well for compounds with boiling points higher than water and azeotrope compositions with more than 50% water (Section 1.2 Method 5031). This work demonstrates excellent response for four alcohols that have boiling points greater than 150°C and azeotrope compositions that are greater than 65% water. These alcohols are 1-hexanol, 1-heptanol, 2-ethyl-1-hexanol and 1-octanol. The two chromatograms below present a 0.1 ppm alcohol standard with and without azeotropic distillation. The response of the alcohols was increased by about two orders of magnitude by the azeotropic distillation. Thus, tracer alcohol analysis at concentrations below the typical 1 ppm limit for direct aqueous injection is possible.

Holding Time Study
A two month refrigerated holding time study is underway. Three different concentration ranges both with and without sulfuric acid preservation are being studied. Initial data shows the tracer alcohols are stable for at least one week in both the preserved and unpreserved samples for most concentrations. Some analyte losses have been observed in the unpreserved samples at the 1 ppm level.

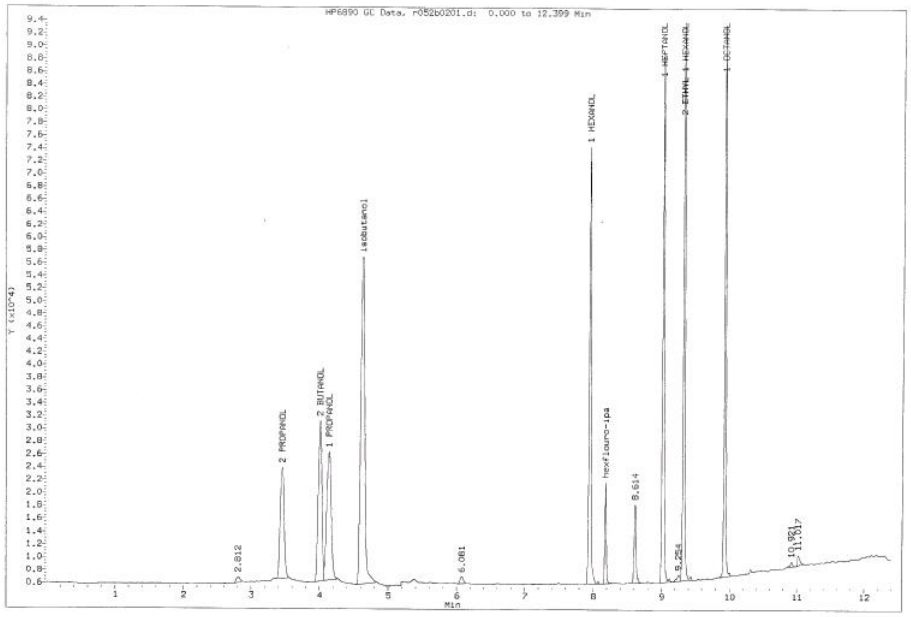


Figure 1. Azeotropic Distillation of 0.1 ppm Tracer Alcohol Standard.

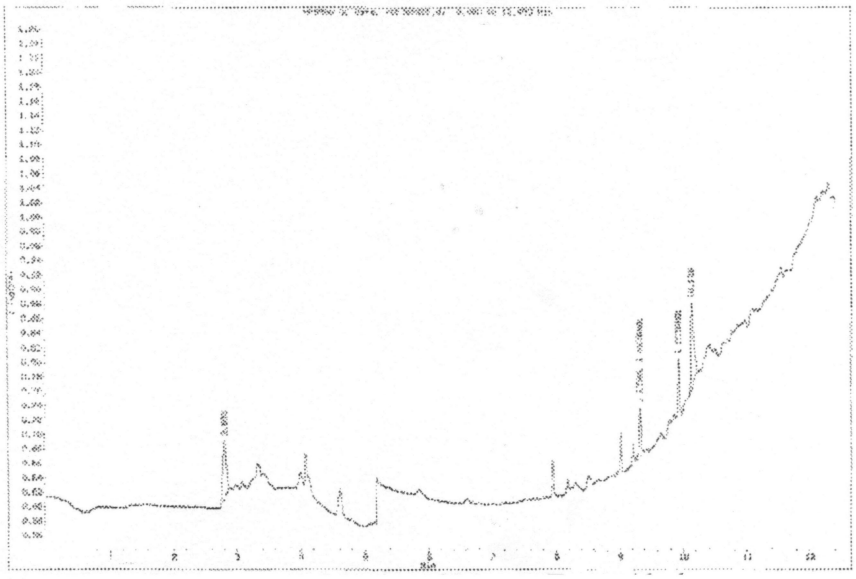


Figure 2. Direct Aqueous Injection of 0.1 ppm Tracer Alcohol Standard.

Summary

The modified Method 5031 successfully separates the tracer alcohol analytes from potential interferences associated with acid preservatives, dissolved salts and surfactants. Recovery of tracer alcohols is generally in the 80-110% range. There are significant losses of the less water-soluble alcohols in high concentration samples in the current process, but dilution of the sample prior to distillation eliminates this solubility limitation. Azeotropic distillation (Method 5031) can be extended to the high-boiling tracer alcohols to allow tracer analysis at concentrations down to 0.1 ppm. The holding time study is underway and demonstrates analyte stability for at least one week for both acid preserved and unpreserved samples. Analyte stability for several weeks is expected.

FAST HIGH RESOLUTION GC FOR ENVIRONMENTAL METHODS: WHAT IS WANTED, WHAT IS AVAILABLE

Dennis R. Gere
Agilent Technologies, Wilmington, DE

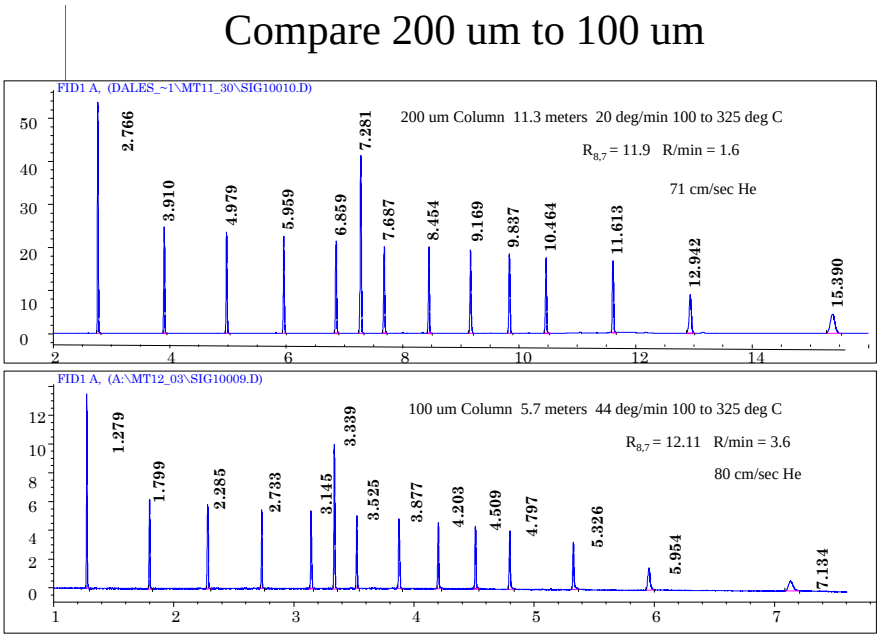
Almost all Environmental labs wish to increase their productivity and or sample throughput, while maintaining the same degree of "goodness" in the results. For many years there has been a tempting siren song out there suggesting that fast gas chromatography may be the answer.

For at least ten years small internal diameter capillary GC columns have been widely available. This usually means internal diameters of 100 micro meters, although other diameters have been suggested such as 50 micro meters.

Within the past two or three years, another approach has surfaced, that is the use of very high temperature programming rates for the column oven temperature. This usually means in excess of 50 degrees per minute up to 300 degrees per minute.

We will show some comparisons and bring in some current opinions about what each of these approaches offers as well as the weaknesses of each. In general, above 50 degrees per minute programming rate, at least two problems present themselves. First, the equipment is less available in most laboratories and the cost of adding such capablility is not trivial. The second consideration, which is perhaps much more limiting is that as one begins to program above 50 degrees per minute, the analysis time decreases as expected, but also the intrinsic resolution drops off considerably and significantly.

Chromatograms will show the limitations of the fast temperature programming. The main conclusion we will present will be to show how GC capillary columns with internal diameters of 200 micro meters may offer most if not all of the desired properties of fast GC. First, we offer that a typical method performed with the conventional diameters of 250 µm to 530 um, can be speeded up by a factor of at least 3X without any loss of resolution. We will also offer up the idea that the 200 µm columns may be operated with most conventional GC equipment, provide robust quantitation, and yield to easy column method translation from conventional methods. Examples will include phthalate esters, organo chlorine pesticides, PCBs and VOCs.



THE PULSED FLAME PHOTOMETRIC DETECTOR FOR THE ANALYSIS OF PHOSPHORUS PESTICIDES IN WASTEWATER AND SLUDGE

Norman A. Kirshen, Senior Chemist
Varian, Inc., 2700 Mitchell Drive, Walnut Creek, CA 94598

Abstract
The Pulsed Flame Photometric Detector (PFPD) was developed recently by Dr. Aviv Amirav of Tel Aviv University, Israel. Unlike the traditional flame photometric detector which has a continuous flame, this pulsed detector operates with a fuel rich mixture of hydrogen and air. This mixture is ignited and then propagates into a combustion chamber three to four times per second where the flame front extinguishes. Carbon emissions and the emissions from the hydrogen/oxygen combustion flame are complete in two to three milliseconds, after which a number of heteroatomic species can give delayed emissions which last up to 20 milliseconds. These delayed emissions, detected by an appropriate photomultiplier tube, are electronically gated to eliminate any background carbon emission and also filtered with an optical filter. While twenty-eight elements can be detected with the PFPD, thirteen give delayed emissions, and therefore infinite selectivity. These latter elements include environmentally important phosphorus. Phosphorus is one of the most sensitive elements detected by the PFPD with a detectivity of 0.1pg/sec, a linear dynamic range of 10^4, and an infinite selectivity versus carbon. This makes it an ideal detector for the detection of phosphorus pesticides when following EPA methods 8141A or 1657.

A series of twenty-eight phosphorus pesticides have been studied using the column confirmation method outlined in the above methods. Injections are made simultaneously into dual capillary columns (30 M x 0.53mm) using an inlet splitter. The columns are each connected to a PFPD. This dual detector approach provides column confirmation via retention times and quantitation values. A series of standards were run and the linearities of the target pesticides determined. Subsequently, a standard extract was analyzed as a calibration check standard. Finally, waste water samples and solid sludge samples were extracted with L/L and ultrasonic extraction, respectively. The results show the occurrence of several common organophosphorus pesticides. The PFPD in the phosphorus mode is demonstrated to have sensitivity and linearity to easily handle the requirements of the two EPA methods.

Introduction

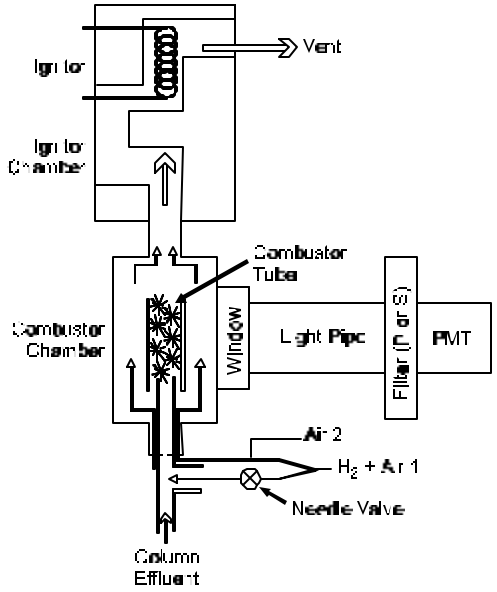
The Pulsed Flame Photometric Detector (PFPD) was developed in the early 1990's by Dr. Aviv Amirav.[1-3] Unlike the traditional flame photometric detector which has a continuous flame, the PFPD is based on a pulsed flame for the generation of flame chemiluminescence. The detector operates with a fuel rich mixture of hydrogen and air. This mixture is ignited and then propagates into a combustion chamber three to four times per second where the flame front extinguishes. Carbon light emissions and the emissions from the hydrogen/oxygen combustion flame are complete in two to three milliseconds, after which a number of heteroatomic species give delayed emissions which can last from four to 20 milliseconds. These delayed emissions are filtered with a wide band pass filter, detected by an appropriate photomultiplier tube, and electronically gated to eliminate background carbon emission. Twenty-eight elements can be detected with the PFPD, thirteen of which give delayed emissions, and therefore infinite selectivity. These latter elements include environmentally and industrially important S, P, As, Sn, and N.

Applications of the PFPD in the Sulfur mode for the analysis of sulfur compounds in petrochemical products as well as in beverages are shown. Several petrochemical applications of interest are as follows: 1) thiophene in benzene, 2) sulfur gases in natural gas, and 3) COS in propylene. The Phosphorus mode of operation is very sensitive and is applicable to the detection of organophosphorus pesticides. High speed data acquisition firmware and software enables one to easily set up the PFPD and to review the pulsed emission data emanating from each chromatogram. This allows the qualitative confirmation of target compounds. Dual channel data processing also provides the ability to qualitatively analyze two elemental modes simultaneously.

Experimental

In a conventional flame photometric detector (FPD), a sample containing heteroatoms of interest is burned in a hydrogen-rich flame to produce molecular products that emit light (i.e., chemiluminescent chemical reactions). The emitted light is isolated from background emissions by narrow bandpass wavelength-selective filters and is detected by a photomultiplier and then amplified. The detectivity of the FPD is limited by light emissions of the continuous flame combustion products including CH*, C_2*, and OH*. Narrow bandpass filters limit the fraction of the element-specific light which reaches the PMT and are not completely effective in eliminating flame background

and hydrocarbon interferences. The solution to this problem, conceived by Professor Amirav of Tel Aviv University was to set the fuel gas (H_2) flow into the FPD so low that a continuous flame could not be sustained. But by inserting a constant ignition source into the gas flow, the fuel gas would ignite, propagate back through a quartz combustor tube to a constriction in the flow path, extinguish, then refill the detector, ignite and repeat the cycle. The result was a pulsed flame photometric detector (PFPD) shown in Figure 1.



The background emissions from the hydrogen-rich air:hydrogen flame (approximately 10 mL/min H_2 and 40mL/min Air) is a broad band chemiluminescence. The combustion of hydrocarbons is highly exothermic, rapid and irreversible, producing a light emission by the hydrocarbon products equal to the time for the flame to propagate through the combustor or 2 to 3 milliseconds. Many of the chemiluminescent reactions of other elements such as S (S2*), P (HPO*), N (HNO*) etc., are less energetic and more reversible, and proceed after the temperature behind the propagating flame has dropped. These heteroatom emissions are therefore delayed from the background emissions. By using the leading edge of the flame background emission to trigger a gated amplifier with an adjustable delay time, heteroatomic emissions can be amplified to the virtual exclusion of the hydrocarbon background emission. The selective amplification of the element-specific emissions is the basis of the PFPD's unique sensitivity and selectivity (see Figure 2).

Figure 1. Schematic Cross Section of the PFPD

The PFPD pulses approximately 3 times per second so that in a period of about 330 milliseconds the detector fills with the mixture of fuel gases and column effluent. When the flame propagates through this mixture, all the light emission from a given flux of some element, sulfur, for example, is concentrated into a period of only 20 milliseconds following each flame pulse. This light intensity is approximately 16 times brighter than the steady state emission from a conventional FPD where the emission would be spread over a period of 330 milliseconds. This effect plus the fact that the gated amplifier is only active during a 20 millisecond period for sulfur combines to greatly improve the signal to noise ratio in the PFPD.

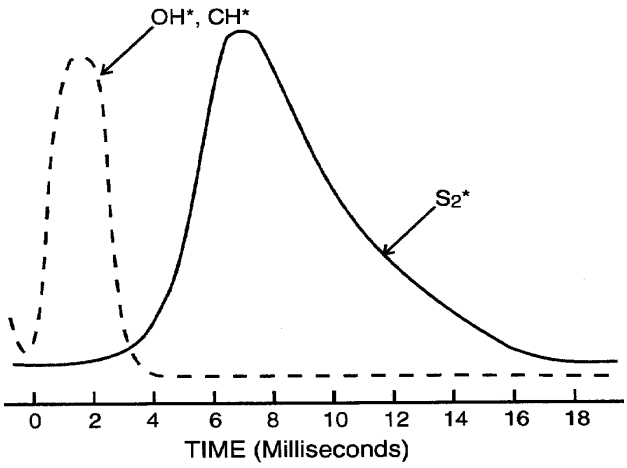


Figure 2. Flame Background and Sulfur Emission Time Profiles

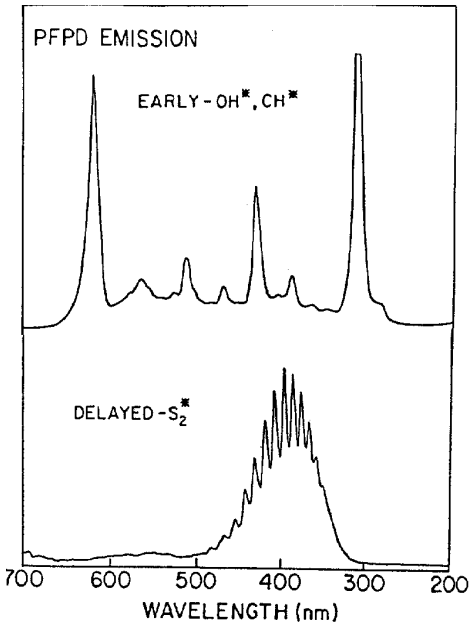
Of equal importance is the ability to resolve the emissions of the heteroatoms from the flame background. The delayed sulfur or phosphorus emissions are integrated after the flame background has dropped to a negligible level. This delay permits the use of much wider bandpass optical filters that no longer must filter the background but can be selected to target the wavelength range of the desired element specific emissions (Figure 3). The result is lower overall noise levels and therefore greater detectivity.

PFPD Specifications

The PFPD detects 28 elements:

S, P N, As, Sn, Se, Mn, B, Br, Ga, Ge, Pb, Si, Te, V, Al, Bi, Cr, Cu, Eu, Fe, Ni, Rh, Ru, W, In, Sb

Thirteen of these elements have delayed emissions from the background Carbon emission and therefore exhibit infinite selectivity:



S, P, N, As, Se, Sn, Ge, Ga, Sb, Te, Br, Cu, In

Control of the PFPD parameters is either from the GC or workstation (Figure 4).

Applications

Application areas of particular interest with the PFPD would include petrochemical, industrial, environmental, and food. Figure 5 shows the separation and detection in sulfur mode of three sulfur gases, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan at 1 ppm each in Natural gas using a Supelco 60M x 0.53mm x 5µM SPB-1 capillary column. This analysis is important since these compounds possess unpleasant odors, are unstable and corrosive and poisonous to industrial catalysts. Figure 6 displays the separation of several sulfur gases in beverage grade CO_2 for which strict standards require the detection of low levels of particular contaminants.

Figure 3. Hydrocarbon and Sulfur Emission Profiles as a Function of Wavelength. Filter used for S is the BG-12.

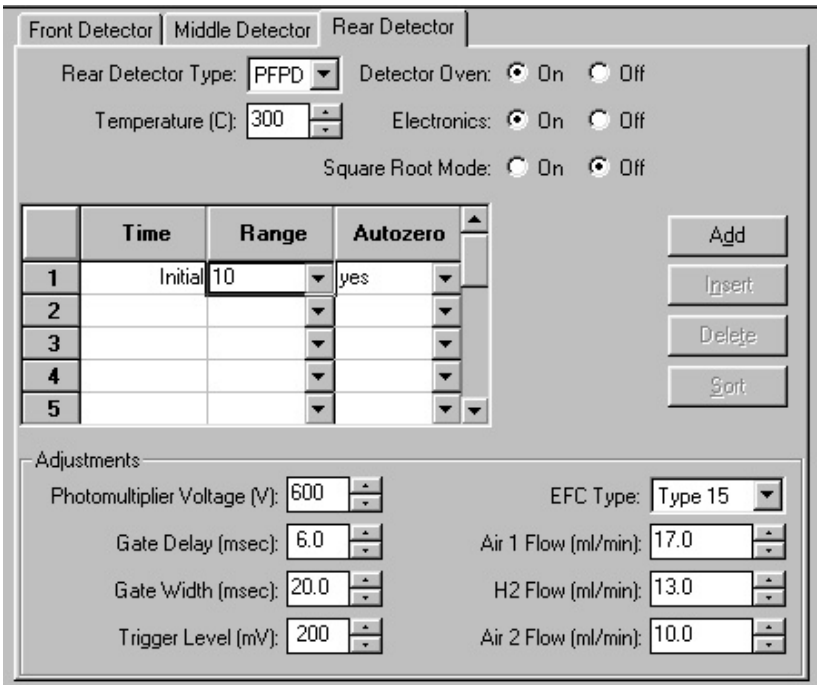


Figure 4. Workstation Control of PFPD

Headspace Solid phase microextraction (SPME) is used to extract sulfur compounds in Beer with a Carboxen™/PDMS fiber and PFPD detection in Figure 7.

Phosphorus detectivity on the PFPD is 0.1 pg/sec or the same as the TSD or NPD detectors but without the peak tailing and with better selectivity toward hydrocarbons and nitrogen compounds. Figure 8 shows a chromatogram of 28 target organophosphorus pesticides being screened in wastewater and sludge by a wastewater treatment plant. Procedures in EPA methods 1657 and 8141A extraction procedures were followed including liquid-liquid extraction for water and ultrasonic techniques for sludge samples. Injections of sample concentrate were directed to dual capillary columns interfaced to dual PFPD's so that column confirmation could be made easily. The columns used were as follows: 1) Primary column, 30M x 0.53mm x 0.5µM DB-608, and 2) confirmatory column, 30M x 0.53mm x 0.5µM DB-1.

The linearity of the pesticides was measured over a range of 30 to 1000 pg/µL. Two of the linearity plots are shown in Figure 9.

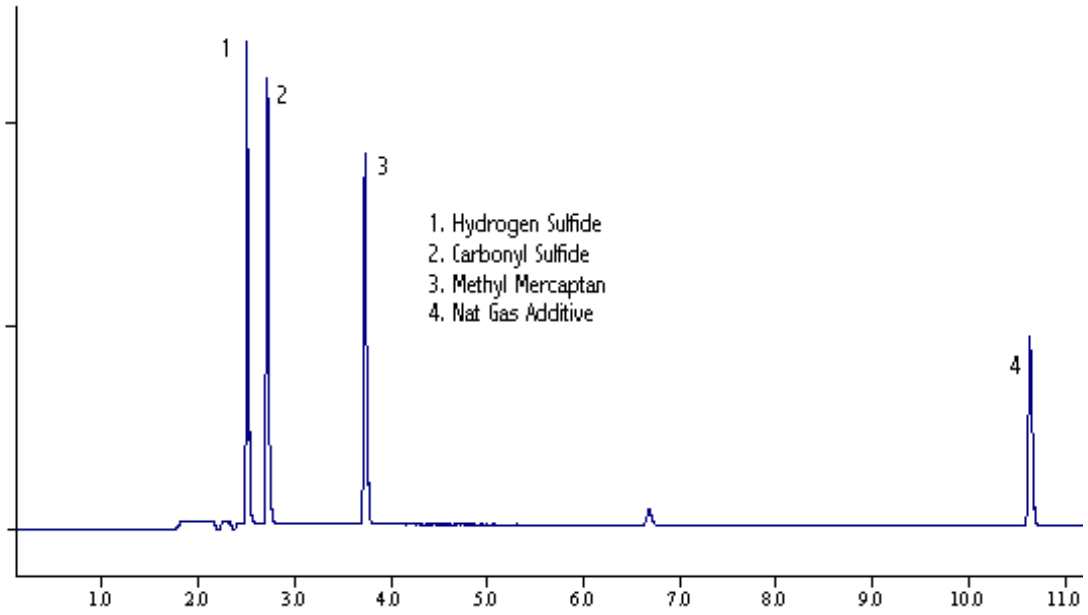


Figure 5. 1 ppm ea. Sulfur Gases in Natural Gas

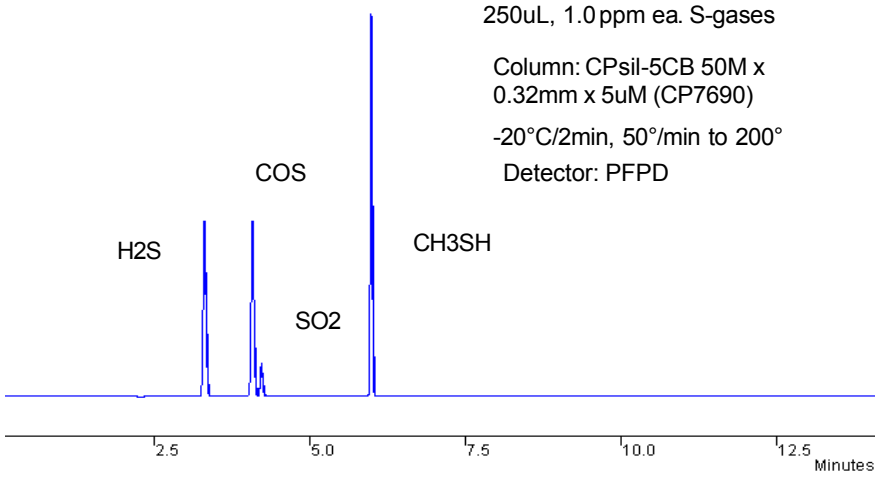


Figure 6. Sulfur gases in beverage grade CO_2.

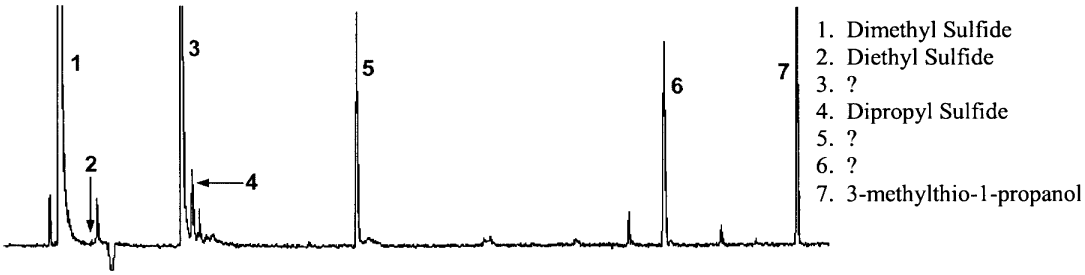


Figure 7. Sulfur Compounds in Beer by SPME

A dual channel chromatogram of a wastewater sample concentrate is shown in Figure 10. Column confirmation by retention time is apparent for Diazinon and Malathion which appear to also have approximately the same peak sizes in the primary and confirmatory columns. Retention time confirmation also is evident for Disulfoton and Trichloronate. On inspection of the quantitative reports for each PFPD data channel (Figure 11), only the results for Diazinon and Malathion are comparable on both channels indicating that they are present in the sample.

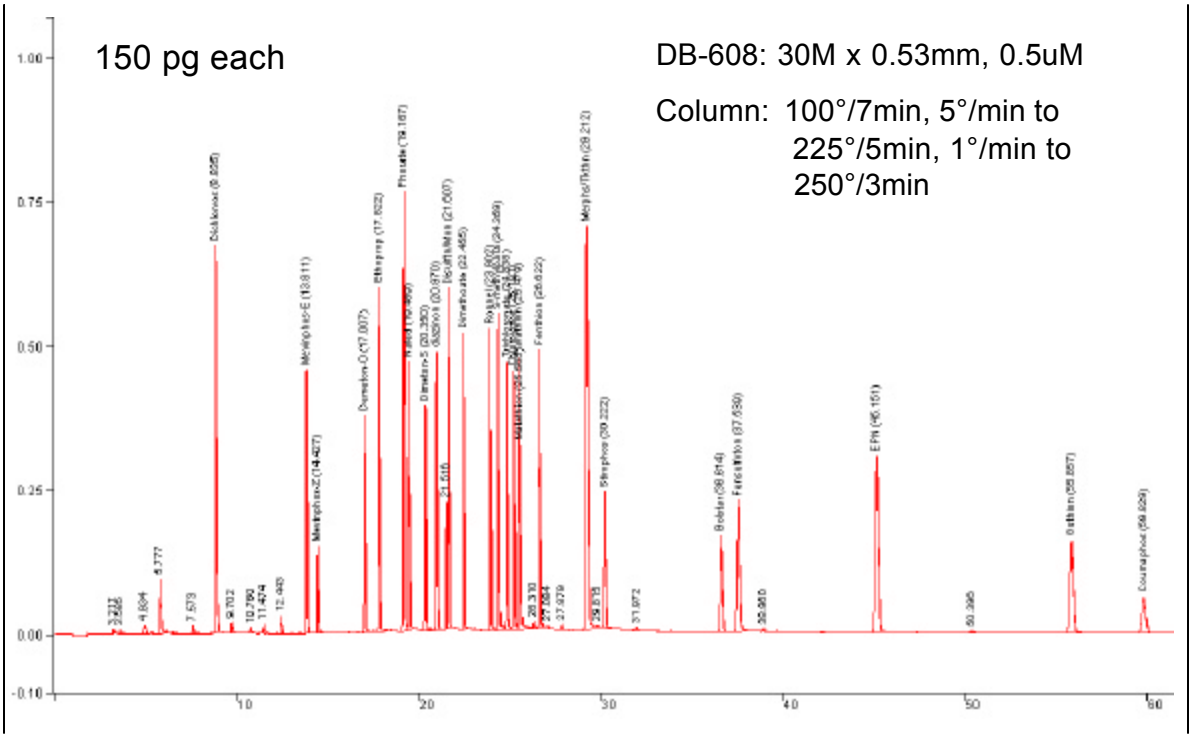


Figure 8. Twenty-eight Organophosphorus pesticides

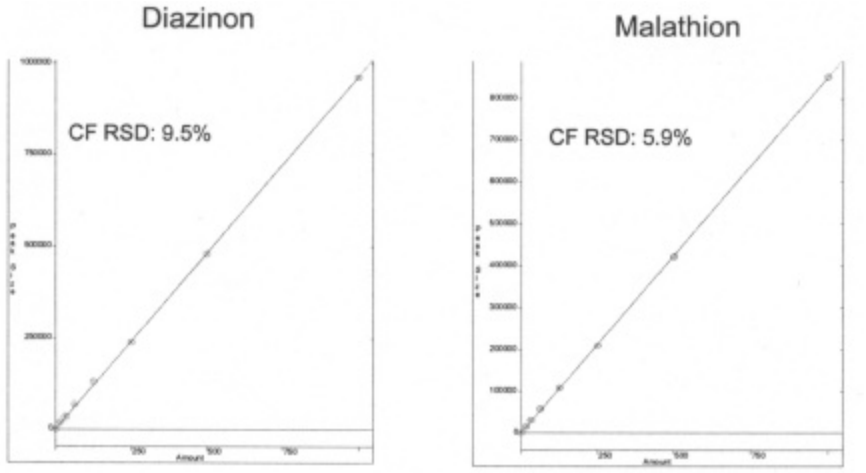


Figure 9. Linearity plots for Diazinon and Malathion from 30 to 1000 pg/uL.

Analytical Software

Analytical software available for the PFPD permits the analyst to view the emissions of the PFPD on a scope like window (Figure 12). This allows for quick set up and optimization of the detector flows. It also allows the user to view the emission profile of the background and eluting peak for qualitative information. Finally, the emission data from the complete chromatogram can be saved as a data file and viewed (Figure 13). The resulting data may also be manipulated to provide dual elemental chromatograms.

Conclusions

The PFPD is a highly sensitive and selective flame photometric detector capable of detecting a number of elements, 13 of these with infinite selectivity. While many applications of the PFPD up to the present have been for Sulfur compounds, the PFPD has excellent sensitivity and selectivity in the phosphorus mode for the determination of organophosphorus pesticides at regulatory required levels. It has been used as the specific detector for wastewater and sludge following EPA methods 1657 and 8141A.

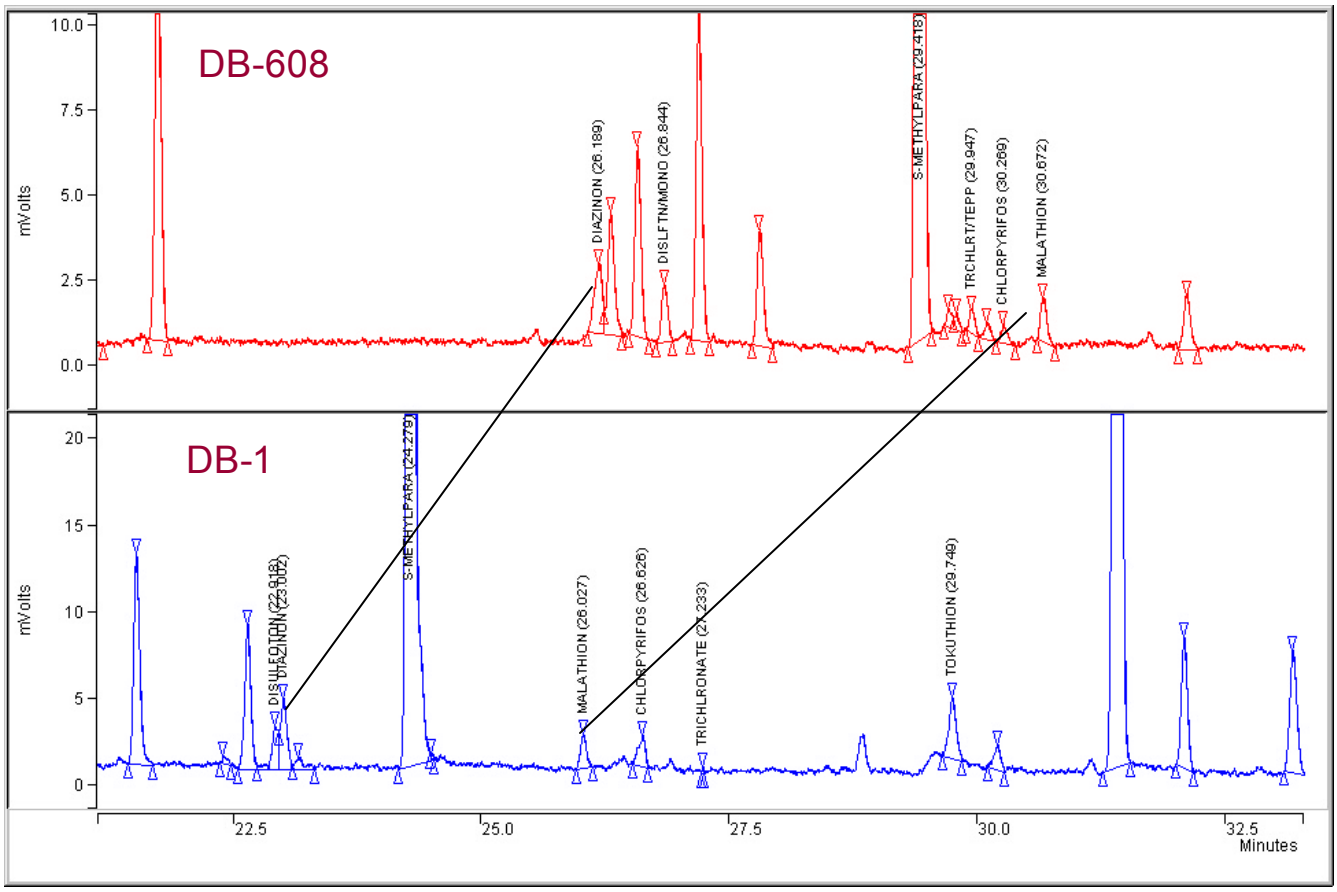


Figure 10.

PRIMARY COLUMN (DB-608)

Peak No.	Peak Name	Result (ug/L)	Time (min)	Offset (min)	Area (counts)	Sep. Code	1/2 (sec)
1	DIAZINON	15.97	26.189	-0.001	11905	BV	5.7
2	DISLFTN/MONO	6.79	26.844	0.125	7654	BB	4.3
3	S-METHYLPARA	679.15	29.418	0.039	623504	BB	3.8
4	TRCHLRT/TEPP	2.37	29.947	0.069	2565	BP	3.4
5	CHLORPYRIFOS	3.31	30.269	0.008	2430	VB	0.9
6	MALATHION	8.09	30.672	0.003	5766	BB	3.8
7	MERPHS/TKTHN	1.89	33.510	0.122	1956	BB	0.0
8	STIROPHOS	5.62	33.929	-0.187	3958	BB	5.0
9	BOLSTAR	32.45	39.140	0.089	24666	BB	8.0
10	GUTHION	52.95	55.576	0.163	22508	BB	12.6

CONFIRMATORY COLUMN (DB-1)

Peak No.	Peak Name	Result (ug/L)	r.t. (min)	Offset (min)	Area (counts)	Sep. Code	1/2 (sec)
1	DISULFOTON	10.67	22.918	0.021	11386	VV	3.8
2	DIAZINON	19.04	23.002	-0.003	18355	VV	5.1
3	S-METHYLPARA	724.35	24.279	0.060	825056	BB	3.7
4	MALATHION	9.68	26.027	-0.003	8238	BB	3.7
5	CHLORPYRIFOS	8.58	26.626	0.196	8549	BB	5.2
6	TRICHLRONATE	0.42	27.233	0.175	399	BB	1.0
7	TOKUTHION	23.31	29.749	0.104	18045	BB	4.3

Figure 11. Dual Channel report for primary (DB-608) and confirmatory (DB-1) columns.

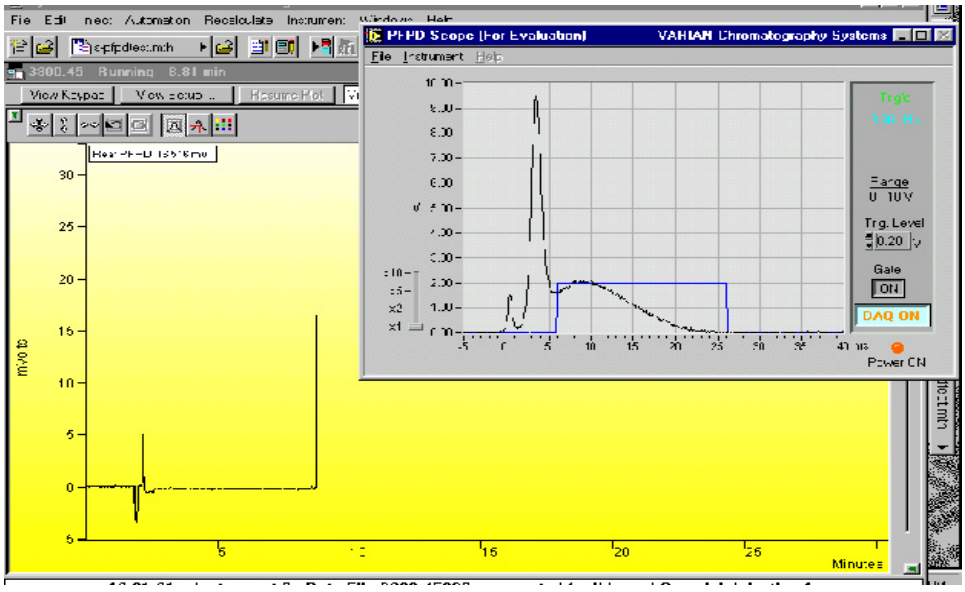


Figure 12.

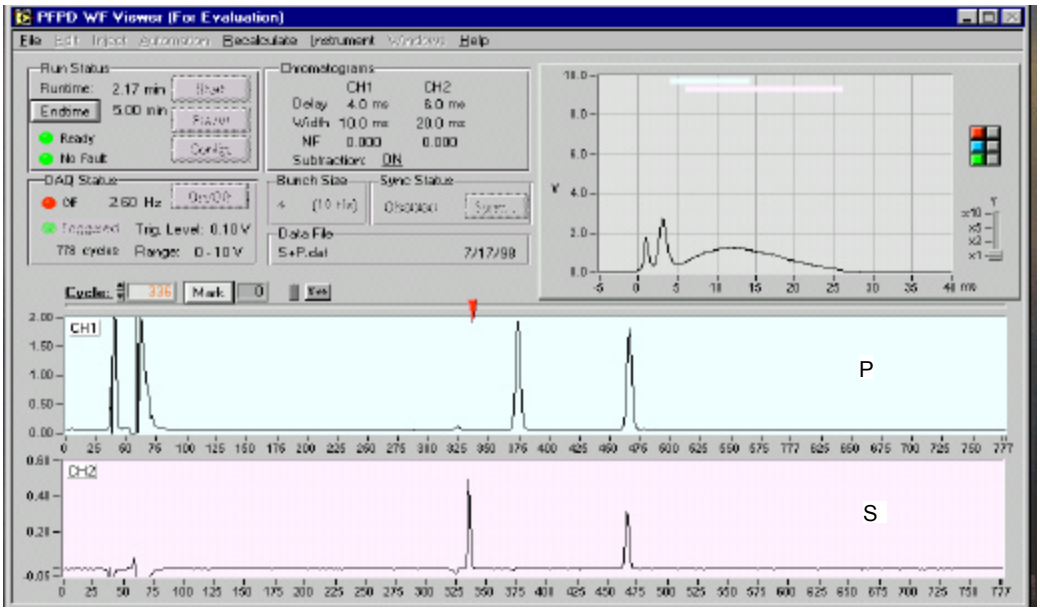


Figure 13. PFPD Data File Viewer Showing Phosphorus and Sulfur Chromatograms

References

1. Amirav, "Pulsed Flame Detector Method and Apparatus". USA, Patent No. 5153673, Israel Patent No. 95617, European patents approved, Japan patent pending.
2. Atar, S. Cheskis and A. Amirav, "Pulsed Flame - A Novel Concept for Molecular Detection", *Anal.Chem.*, **63**, 2061-2064 (1991).
3. Cheskis, E. Atar and A. Amirav, "Pulsed Flame Photometer - A Novel Gas Chromatography Detector", *Anal. Chem.*, **65**, 539-555 (1993).

THE EFFECT OF HYDROGEN CARRIER GAS IN THE GC/ECD ANALYSIS OF ORGANOCHLORINE PESTICIDES

C. Eric Boswell
National Air and Radiation Environmental Laboratory, US Environmental Protection Agency,
540 South Morris Avenue, Montgomery, AL 36115-2601
(334) 270-7071
boswell.eric@epa.gov

With the emphasis on performance-based measurement systems (PBMS), GC analysts in environmental laboratories have many options available to them in configuring instrumentation. When attempting to maximize the benefits of modern GC instrumentation, analysts must not forget basic principles of gas chromatography. The van Deemter equation suggests that hydrogen would provide improved column efficiency over helium in terms of plate height at a given linear velocity. If satisfactory separation is achieved with helium, the use of hydrogen should accomplish the same separation in less time. At the National Air and Radiation Environmental Laboratory (NAREL), we substituted hydrogen for helium carrier gas in the GC/ECD analysis of organochlorine pesticides. This poster compares both the column efficiency (peak separation) and analysis time of organochlorine pesticides when helium carrier gas was replaced by hydrogen. We learned that classical principles of gas chromatography were as important as new instrumentation when we evaluated SW846 Method 8081 for overall efficiency. The optimum linear velocities approximated using van Deemter curves do, in practice, provide a reliable estimate of column efficiency when using hydrogen as a replacement for helium.

We addressed the two major concerns about the use of hydrogen: expense and safety. The solution to both concerns was found in using a hydrogen generator rather than a traditional gas cylinder. The hydrogen generator produces high purity gas (99.999+%) and, after an initial payback period, costs less than hydrogen cylinders. Safety issues about the use of hydrogen were also resolved because hydrogen storage capacity in a generator is minimal (only 50 mL). When considering ways to improve overall efficiency in our GC/ECD analysis of organochlorine pesticides, we found hydrogen carrier gas provided a means to improve peak resolution and reduce analysis times. After optimization, this change in carrier gas proved to be a cost-effective option to improve the GC/ECD analysis of organochlorine pesticides by SW846 Method 8081.

INTRODUCTION

When attempting to maximize the benefits of modern GC instrumentation, analysts must balance their desire to improve the efficiency of an analysis with pragmatic concerns: (1) cost, (2) use of standard consumables, and (3) safety of new procedures. At the NAREL we wanted a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 15 minutes, very low Endrin/DDT degradation, and good resolution on difficult analyte pairs. We also wanted the resulting chromatographic system to be one that was easy and safe to use by any reasonably trained analyst.

We configured a GC with dual pressure programmable injectors, two dissimilar 0.53 mm capillary columns, and dual ECDs. Although most of the work was in installing a hydrogen generator, there were other parameters to optimize. For example, we chose a relatively high initial oven temperature to reduce the cycle time of the analysis. We also adjusted the detector makeup gas flow to achieve acceptable sensitivity. We adjusted the injector pressure program to accommodate the higher liner velocity of hydrogen. In our dual injector system, we kept the injector pressures similar during injection and programmed them differently after the split valve opened to achieve chromatographic resolution. We chose a compromise initial oven temperature that was hot enough to keep the GC cycle time short and low enough to prevent the earliest eluting compounds from tailing too much. This is different from the classical splitless injection technique where the initial oven temperature is kept low until most of the sample can slowly migrate from the inlet sleeve to the head of the column. This deviation from classical splitless injection used both the principles of solvent focusing and high pressure injection to achieve the desired goal. The result was a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 15 minutes, very low Endrin/DDT degradation, and good resolution on difficult analyte pairs.

EXPERIMENTAL

A mix containing twenty pesticides, two surrogate standards, and three internal standards (Ultra Scientific) was prepared from the dilution of certified standard mixes with pesticide grade hexane (Burdick & Jackson). Our experimental results are best discussed in terms of injection technique, pressure programming, and oven temperature programming.

We decided to use splitless injections rather than direct injections to both simplify routine maintenance and increase system ruggedness. Using a 4 mm ID single taper inlet liner eased routine column maintenance because the insertion distance of the column into the liner was the only critical step. A 1.0 µL volume of hexane extract will expand to approximately 250 µL of vapor at 5.8 psig. This is easily contained within the 900 µL of available volume in a 4mm ID liner. We found that a pressure increase after injection provided two benefits: (1) the vapor cloud moved onto the analytical column in a smaller plug and (2) the compounds were pushed through the column quicker. We chose 5.8 psig as the initial injector pressure which resulted in a column linear velocity of 99.9 cm/sec. We used 120ºC as our initial oven temperature. These represent a compromise between classical solvent focusing and high pressure injection. Moving the sample vapor cloud onto the column quickly has several benefits. Along with keeping early eluting peaks from tailing, high pressure injections dramatically reduce Endrin/DDT degradation. Combined Endrin/DDT degradation rarely exceeds 5.0% with this configuration. Optimization of the opening and closing times for the split vent are still crucial for quantitative accuracy.

We chose a linear velocity above the optimum linear velocity for hydrogen to eliminate peak tailing. Table 1 contains the pressure program. Although the carrier is operating above the optimum linear velocity for hydrogen, an empirically-determined compromise was reached between analysis time and chromatographic resolution. We addressed the safety concern about the use of hydrogen by installing a hydrogen generator. Safety issues about the use of hydrogen have been largely resolved because the hydrogen storage capacity in a generator is minimal (only 50 mL).

Table 1. Chromatographic Conditions

GC Parameter	Value
Carrier Gas	Hydrogen
Injector	Splitless, 1µL, Purge Delay 0.25 min. Inlet Temperature 250ºC
Pressure Program	Initial Linear Velocity:99.9 cm/sec. @120ºC Rtx-5 5.8 psi Hold 0.25 min. to 20.7 psi @ 99 psi/min. Hold .25 min. to 5.8 psi @ 50 psi/min. to 14.0 psi @ 1.0 psi/min. Hybrid 5.8 psi Hold 0.25 min. to 20.7 psi @ 99 psi/min. Hold 3.00 min. to 5.8 psi @ 50 psi/min. Constant Flow
Temperature Program	120ºC Hold 0.25 min. to 150ºC @ 60ºC/min. to 200ºC @ 8ºC/min. to 285ºC @ 40ºC/min. Hold 1.0 min.
Detector	N_2 Makeup @ 100 mL/min. Anode Purge @ 10mL/min. ECD @ 310ºC

The GC oven temperature program is also given in Table 1. The temperature program was optimized to separate critical pairs such as Endosulfan I/alpha Chlordane and Dieldrin/DDE on the Rtx-5 column and Heptachlor epoxide/ gamma-Chlordane and Endosulfan II/DDT on the confirmation column.

SUMMARY

At the NAREL we wanted a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 15 minutes, very low Endrin/DDT degradation, and good resolution on difficult analyte pairs. We also wanted the resulting chromatographic system to be one that was easy and safe to use by any

trained analyst. Although most of the work was in installing a hydrogen generator, there were other parameters to optimize. We deviated from classical splitless injection technique slightly to accommodate the use of pressure programmable injectors. This deviation from classical splitless injection used both the principles of solvent focusing and high pressure injection to achieve the desired goal. The result was a GC method for twenty-two of the organochlorine pesticides on the Method 8081 list with a run time of less than 15 minutes, very low Endrin/DDT degradation, and good resolution on difficult analyte pairs.

TAKING ADVANTAGE OF NEW TECHNOLOGY IN GC/MS VOLATILES

Patrick Conlon, Director of Quality and Technology
STL Pittsburgh, 450 William Pitt Way, Pittsburgh, PA 15238

The presentation will consist of a discussion of the following:

1. An overview of performance characteristics of Archon autoanalyzers/Tekmar3000/HP-5973s for SW-846 & CLP Methods, including Standard & Low Level Methods. 524.2 may be added if time allows.

2. A summarization of the strong points and weak points of these new instruments. The strong points being linearity, sensitivity, maintaining calibration and reliability. All classical measures of instrument performance. The weak points being RRFs and SPCC performance which derive from the CLP tradition. These measure of performance (RRF & SPCC) derive much of their values as performance measures within the framework of the instruments and methods being used at the time of the method creation. This section would close with examples of how the new analytical systems may provide outstanding performance. Performance that may not be well reflected by some traditional performance measures. So isn't this where PBMS fits in?

3. A summary, which includes a short discussion of definition and value of PBMS and its inherent conflict with data validation which by its nature presses for traditional measures and forms of compliance.

Closing comments would include that there are outstanding instruments available for doing both updated versions of conventional analysis and entirely new technologies. And that while PBMS is very valuable in its facilitation of the implementation of "new" technologies, it does not appear to be, nor should it be a substitute for updating traditional methods to accommodate updates in traditional technology.

SELECTION OF A TOC ANALYZER: ANALYTICAL CONSIDERATIONS

Joe Furlong, Product Line Manager, Bob Booth, Senior Research Chemist and Brian Wallace, Application Chemist

Abstract
The task of choosing a Total Organic Carbon analyzer brings one to consider the many instruments currently on the market. This becomes more difficult when faced with understanding that TOC analyzer manufacturers may use different oxidation techniques which could effect the analytical data. This article highlights some analytical differences between the two major TOC oxidation techniques and offers suggestions for a process to base the choice upon the user's unique needs.

Introduction

Since the relationship between BOD, COD, and TOC was established in the late 1970s, TOC analyzers have become an analytical backbone in many water treatment and quality control laboratories worldwide. Typical applications and levels of TOC in various water streams can be seen in Table 1. Important environmental and pharmaceutical regulations such as US EPA's Information Collection Rule and United State Pharmacopoeia (USP) TOC in Water for Injection (WFI) have only increased the importance of the measurement.

Table 1

Type of Water	TOC (mg/l)
High Purity Water	<0.01
Water for Injection	<0.50
Ground Water	<1
Seawater	<1
Drinking water	<4
Surface water	<10
Wastewater	>10

Over the years many TOC analyzers have been introduced by various manufacturers which use different oxidation technologies. The development of different oxidation technologies were used to gain an analytical and marketing advantage against a competitive manufacturer. Currently, two major oxidation technologies dominate the TOC market place: combustion and UV/persulfate. The late 1980s saw the start of a major debate between which technique was best suited for testing for TOC. This paper is designed to highlight the advantages and disadvantages of both techniques in a balanced and analytical manner. This will give users appropriate information to make an informed decision as to which technique serves their needs the best and explain disparities between the two techniques.

Methods

Official methods are well defined in their requirements as described in Table 2. All TOC analyzers today convert the organic carbon in the sample to carbon dioxide. The technique of detecting the resulting carbon dioxide varies and some detection techniques are not in all official methodologies.

Table 2

Oxidation	Detection Technique	Analytical Range	Official Methods
Combustion	TCD	0.5% to 100%	AOAC 955.07
Combustion	Coulometric	1% to 100%	ASTM D4129
UV/Persulfate	NDIR	0.002 to 10,000 mg/l	EPA 415.1, 9060A Standard Methods 5310C ASTM D2579, ISO (Draft) 8245, AOAC 973.47, USP 643
Heated Persulfate	NDIR	0.002 to 1,000 mg/l	EPA 415.1, 9060A Standard Methods 5310C ASTM D2579, ISO (Draft) 8245, AOAC 973.47, USP 643
Combustion	NDIR	0.004 to 25,000 mg/l	EPA 415.1, 9060A Standard Methods 5310B ASTM D2579, ISO (Draft) 8245, AOAC 973.47, USP 643
UV/Persulfate	Membrane/Conductivity	0.0005 to 50 mg/l	Standard Methods 5310C, USP 643
UV	Conductivity or NDIR	0.0005 to 0.5 mg/l	USP 643

Analysis Range

The range of TOC measurement varies with oxidation method and detection technique. A combustion/TCD method, used in Tekmar-Dohrmann's CHNS&O analyzer, may measure up to 100% carbon in a sample, whereas the NDIR and conductivity detectors vary in range from as low as 0.5ppb to 25,000ppm. Some NDIR detectors give the advantage of sensitivity to low amounts of TOC while not sacrificing the ability to analyze widely varying concentrations without numerous cal- ibrations. The conductivity detectors are capable of measuring very low

levels of TOC. However, they require dilutions to measure many environmental samples and are sensitive to various interferences such as chlorides and other ionic chemicals.

Picture 1. Apollo 9000 Combustion TOC Analyzer w/ Autosampler

Oxidation Techniques

All TOC analyzers offered today are either the combustion method or low-temperature oxidation. The low-temperature oxidation is a chemical oxidation aided by 100°C heat and persulfate, UV and persulfate or only UV irradiation. The purpose of the oxidation step is to convert the organics to carbon dioxide. Then, a detector measures the amount of carbon dioxide and applies that result to a calibration curve to get the TOC value.

First, to measure TOC, all TOC analyzers either remove or measure the inorganic carbon (IC), defined as dissolved carbon dioxide, carbonate, and bicarbonate. One common technique is to introduce the sample and a small amount of 20% phosphoric acid to an inorganic reaction cell. The sample is usually sparged with carrier gas to drive off any IC.

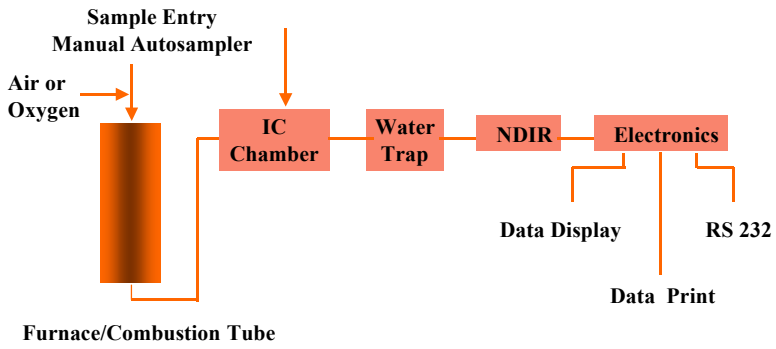
Combustion Oxidation Technology

The combustion technique uses heat (680°C) or higher, in a stream of air, oxygen or nitrogen and usually in the presence of a catalyst. Dissolved organics and particulate organics are expected to oxidize fully to carbon dioxide under these conditions. The catalysts vary from cupric oxide, cobalt oxide or platinum on an alumina support. The Tekmar-Dohrmann Apollo 9000, as seen in picture 1, uses combustion from 680°C to 1000°C, depending upon the application, with a proprietary catalyst. Fig. 1 is a basic combustion TOC block diagram.

Persulfate and other Wet-Chemical Oxidization Technology

There are three low-temperature techniques, and particulate matter in a sample presents a problem to all of them. Usually the particulates are more difficult to oxidize by nature or organics escape exposure to the reagents by being within the interstitial spaces of the particles. High molecular weight compounds such as proteins may be slow to oxidize with the low temperature techniques.

Figure 1



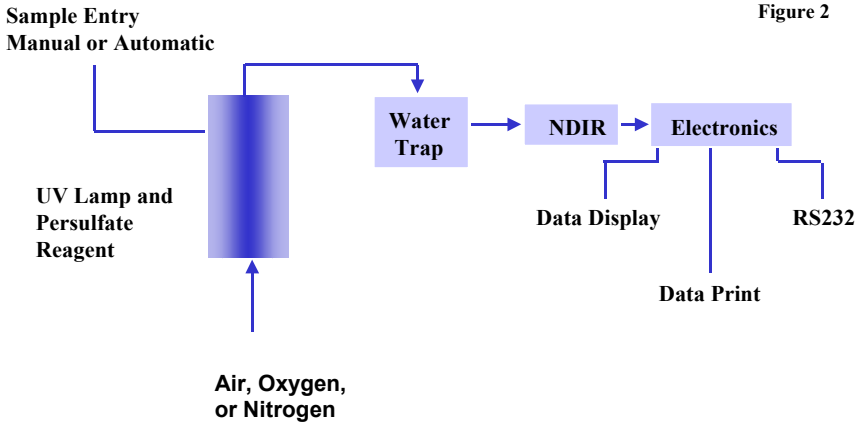


Figure 2

The low-temperature techniques have the advantage of allowing a large volume of sample to be analyzed thereby improving the low limit of detection. Also the blank value is very low as long as the reagents are pure, which makes the analysis more accurate.

a. Ultraviolet irradiation. In this technique, the sample is exposed to UV light from a mercury vapor lamp. With sufficient time of exposure, all the dissolved organics may be oxidized to yield CO_2.

Detection of the CO_2 is usually by the change in conductivity of the sample. The maximum amount of TOC practically measured is 1 ppm and different organics require different times to be fully oxidized. The Tekmar-Dohrmann Phoenix 8000 uses this technique with NDIR detection for ultra-low TOC analysis.

b. Heated persulfate. The sample is mixed with a quantity of persulfate solution and heated to 100 C. After a set period of digestion time, the resulting CO_2 is purged out by a carrier gas and detected by NDIR. The oxidation is much more vigorous than UV only. However, the digestion time still needs to be optimized for complete oxidation.

c. Persulfate plus UV irradiation. The sample is simultaneously exposed to persulfate, UV radiation and resulting CO_2 is purged out by a carrier gas and detected by NDIR. The oxidation is significantly enhanced over UV-only and persulfate only methods by simultaneous ionization of dissolved organics and the production of highly reactive sulfate free radicals and hydroxyl free radicals. This process also insures that all available organic carbon is oxidized without worry about optimization. The Tekmar-Dohrmann Phoenix 8000 uses this technique for most applications.

The CO_2 in b) and c) is detected in one of two ways: 1) by allowing it to permeate a membrane into a low conductivity water stream and thereby change its conductivity, or 2) purging the CO_2 to an NDIR. The Tekmar-Dohrmann Phoenix 8000 uses a NDIR. By purging the CO_2 while continuing the UV/persulfate reaction, the vigor of the reaction can be observed in the detector response.

The UV/Persulfate technique of the Phoenix 8000 allows true parts per billion measurement of TOC. It stands on the proven history of UV/persulfate TOC in the Dohrmann DC-54, DC-80 and DC-180 analyzers. The ease of handling up to 20 mL of sample means that the detection limit is in the range of 1 to 2 ppb C. The blank of the system is the contribution from the persulfate reagent. Since the volume of reagent is 1/40th that of the largest sample volume, the contribution is indeed very small. Samples that have extremely low carbon can be analyzed without the addition of persulfate and thus the blank is reduced even further. Figure 2 is a typical UV/Persulfate flow diagram.

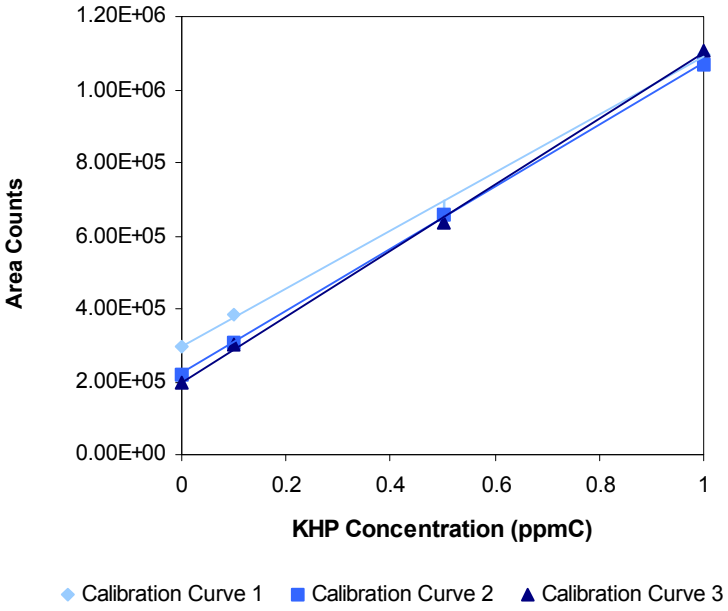
Analytical

There are four TOC analytical parameters that are extremely important to consider when choosing a TOC analyzer. They are instrumental background, recovery, particulates, and detection limits.

Instrumental Background

In general this analytical parameter is only important for the low level measurement of TOC such as surface, drinking, high-purity water and water for injection (WFI). Therefore, most users measuring TOC in industrial water effluent need not to worry.

Instrumental background, sometimes called blank contribution, is the carbon contribution inherently associated with the TOC analyzer. Some sources of instrumental blank are the catalyst used in combustion based TOC analyzers, persulfate or acid used in wet chemistry based TOC analyzer and dilution water[1]. The amount and stability of the blank has a major impact on a TOC analyzer's detection limits and reproducibility.



UV persulfate instrumental background to sample analysis is well known to be smaller in proportion to that of the other major technique, combustion TOC analysis. As Standard Method 5310 states about selection of a method, "The high-temperature methods accumulate nonvolatile residues in the analyzer, whereas, in Method C (The Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method), residuals are drained from the analyzer. Method C (The Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method) generally provides better sensitivity for lower-level (<1mg/L) samples."[2] This accumulating effect on the blank for the combustion method of detection yields a shifting unstable blank, as seen in Figure 1. These accumulating effects are from residual organics from

the samples, which can add to the results. On the other hand, the UV persulfate blank is more stable, utilizing its ability to remove the residuals from the analyzer. Thus, the UV persulfate method has a smaller blank contribution during sample analysis compared to that of the combustion method. Therefore, the combustion blank is somewhat of a moving target for low level analysis whereas the UV persulfate blank is a cleaner more consistent blank[3].

Recovery

This analytical parameter has been hotly debated for the past 15 years. Many studies have been done that compared persulfate against combustion using different "tough" to oxidize compounds. Many of these reports seem to conflict with each other's results. However, some conclusions can be drawn from the reports.

- There is no question that combustion TOC analyzers give more consistent recoveries than persulfate.
- Humic acid seems to be the most challenging compound to analyze. Other than being difficult to oxidize, is it also difficult to find humic acid with a carbon content that has been accurately measured and keep in solution in high concentrations. These factors alone would adversely effect analytical results and conclusion.
- The higher concentration of persulfate increases recoveries for difficult to oxidize compounds[4].
- The newer generation of UV/Persulfate TOC analyzers achieve much higher recoveries than older generation analyzers due to advances in UV lamp design and higher concentration of persulfate[4].

			DC-190			
Compound	50 ppm	RSD	%recovered	10 ppm	RSD	%recovered
Isonicotinic Acid	48.73	1.31	97.5	9.589	2.754	95.9
Hexane-Sulfonic Acid	46.35	1.396	92.7	9.202	0.841	92.0
L-Glutaric Acid	48.3	2.479	96.6	9.578	0.771	95.8
Citric Acid	49.5	0.909	99.0	10.05	1.413	100.5
Lignosulfonic Acid	43.24	0.285	86.5	9.005	0.482	90.1
L-Tryptophan	47.76	1.518	95.5	9.517	2.435	95.2
Humic Acid	45.63	1.619	91.3	9.011	3.232	90.1
1,4-Benzoquinone	46.94	2.735	93.9	9.814	5.792	98.1
		average =	94.1			94.7
			Phoenix 8000			
Compound	50 ppm	RSD	%recovered	10 ppm	RSD	%recovered
Isonicotinic Acid	51.021	0.94	102.0	9.29	0.06	92.9
Hexane-Sulfonic Acid	47.558	0.62	95.1	9.097	0.22	91.0
L-Glutaric Acid	48.584	1.5	97.2	9.443	0.33	94.4
Citric Acid	48.642	1.83	97.3	9.512	0.65	95.1
Lignosulfonic Acid	47.343	0.28	94.7	9.389	0.18	93.9
L-Tryptophan	45.401	2.22	90.8	8.9663	1.45	89.7
Humic Acid	40.9	2.41	81.8	9.042	0.82	90.4
1,4-Benzoquinone	46.65	0.35	93.3	9.043	0.08	90.4
		average =	94.0			92.2

Miller's paper *Comparison of Combustion versus UV/Persulfate TOC Analysis* appears to draw the best conclusion. His data and observations report that both techniques, using the DC-190 combustion TOC analyzer and Phoenix 8000 UV/Persulfate TOC analyzer, gave reasonably good agreement across many different difficult to oxidize compounds as seen data in table 3. However, the UV/ Persulfate technique showed lower recovery than the combustion TOC analyzer above 10 ppm. He concludes that when particulates are present in the 50 ppm concentration of humic acid, the persulfate technique is less efficient in handling particulated samples[5]. More on particulates later on in this paper.

Particulates

One of the most challenging matrices to analyze is a particulated matrix, which is commonplace in wastewater sites. The presence of particulates can lead to heterogeneous sampling resulting in bad reproducibility and accuracy, and clogging of lines and valves in contact with the sample. This concern is minimized by letting the sample pass through a filter as stated in Standard Method 5310C. However, this method excludes the TOC contributed by the particulates that were filtered, therefore reporting the value as dissolved organic carbon (DOC). Many European communities do not allow the filtering of the sample. They are so concerned about the particulate organic matter that they have developed an analytical method, ISO/FDIS 8245, to validate an instrument's ability to measure samples with particulates.

It is generally accepted that the persulfate oxidation technique gives low recoveries on particulated organic matter. Consequently, this technique reports DOC values, but many analytical communities accept this value as TOC depending on the nature of the sample, such as drinking water and water for injection. The combustion technique excels at the measurement of particulate organic matter, but caution needs to be exercised since the instrumental sampling technique and instrumental options can give varied results from instrument to instrument. Dr. Theresa

Lee-Alvarez reports in her paper *Total Organic Carbon Analysis of Particulated Samples*[6] that a number of factors play an extremely important role in the accurate measurement of TOC with particulated organic matter. They are instrumental sample handling, sample stirring, and sample volume injected. The data presented in table 3 is an excellent example of the TOC values reported between an Apollo 9000 combustion TOC analyzer from Tekmar-Dohrmann that has been properly optimized to measure particulated organic matter (column 2) and one that was not (column 1).

Table 3

Sample	Column 1		Column 2	
	TOC (ppmC)	% RSD	TOC (ppmC)	% RSD
100 ppmC KHP	104.1928	1.51	99.0726	2.87
20 mm cellulose	83.6335	2.57	100.5933	0.31
(100 ppmC)	81.9835	3.55	101.8094	3.18
20-75 mm cellulose	66.4405	6.92	90.2088	3.42
(100 ppmC)	64.7105	4.35	90.7908	5.44

Detection Limits

Applications that require low TOC measurement, 1 ppm or less, demand a TOC analyzer with a very low instrument background and large sample injection.

Instruments that use UV, UV-persulfate or heated persulfate oxidation typically show low background characteristic. Even drinking water methods, generally not considered as low level, recognize this important issue as stated by Standard Method 5310 discussed earlier in this paper. Consequently, the primary disadvantage of the combustion TOC is the magnitude of the blank value. This response may be due to any organic material that is washed from the combustion train by the vaporized sample or even the catalyst itself. The accuracy of a 1 ppm or less measurement of TOC is therefore compromised. Other combustion TOC manufacturers have recognized instrumental blank as a problem. They have recommended procedures and special options to lessen the instrumental blank such as special high sensitivity catalyst and lengthy blank checking procedures. The Apollo 9000 combustion TOC from Tekmar-Dohrmann has a proprietary catalyst with an inherent low blank and an automated blank measurement that takes about one hour to complete.

Picture 2. Phoenix 8000 UV/Persulfate TOC Analyzer

The advantage is also given to the persulfate technique since it can analyze up to 20 mL of sample. This increases the amount of organic carbon to be detected therefore decreasing the detection limit. Typically, as little as 4 mL of analyte is needed for the Phoenix 8000, as seen in picture 2, to reach an IDL of 7 ppb[7]. The combustion technique has a limited volume of sample that can be injected since large injection volumes cool the catalyst. Two milliliters of sample is typically the limit.

While combining the variability of the instrumental blank with the power of sample volume, low level TOC analysis is easier using the persulfate technique versus the combustion technique. This is not to say low level analysis cannot be done with a combustion TOC analyzer, it is just more difficult.

Recommendations

Below are typical applications and recommendations for which TOC oxidization technology would give the best

analytical results. Please be advised that there are exceptions for every application. In the sprit of keeping our recommendations to the point, we will refrain from commenting on every exception.

High Purity Water – UV or UV/Persulfate

Comments: These are samples with less than 50 ppb TOC. Combined with the trouble free operation and the ease of detecting very low level TOC, UV or UV/Persulfate is, by far, the best choice.

Water for Injection – UV or UV/Persulfate

Comments: These are samples with less than 500 ppb TOC. The combustion technology can measure TOC in this range, but UV or UV/Persulfate is still the easier oxidation technology to use for this application.

Drinking or Source Water – UV/Persulfate or Combustion

Comments: UV/Persulfate would be my professional choice. Meeting precision and accuracy requirements for low level calibration check standards, such as 0.50 ppm, is still easier with the persulfate technology. However, if capturing the particulated organic matter in the TOC value is important, then combustion would be the better oxidation technology.

Salty Waters – Combustion

Comments: Not discussed in this paper, the combustion oxidation technology is not affected by the chlorides present in seawater and other salty water matrixes[8].

Industrial Waste Effluent – Combustion

Comments: Particulates, chlorides, and tough to oxidize compounds are the type of challenging matrixes that the combustion oxidation technology was designed to handle.

Conclusion

This study shows that the best TOC oxidation technology is the one which meets the application and analytical needs of the situation. Also, each oxidation technology has its own advantages and disadvantages. Therefore, when faced with the tough decision of which TOC analyzer to purchase, I would recommend using the following road map. First, one must decide what is the primary analytical application. Second, outline the analytical needs that must be met. Third, use the above guide to choose the TOC oxidation technology. Finally, interview the appropriate sales representative to determine the feature set that works best for your analytical needs. The choice is yours.

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CURRENT MEASUREMENT CAPABILITIES FOR ENDOCRINE DISRUPTING COMPOUNDS

Zoe Grosser, Elaine LeMoine and Ruth Wolf
PerkinElmer, 50 Danbury Road MS-219, Wilton, CT 06897

ABSTRACT
Endocrine disrupting compounds have been identified as a new category of environmental contaminants. Many of the compounds that have been identified as potential endocrine disruptors have been listed previously as contaminants under existing regulatory programs. The concentration levels of concern have been set for toxicity, based in many cases upon potential carcinogenicity. Lower concentrations may however, disrupt endocrine functions by causing chronic or serious effects that are not observed until subsequent generations.

Analytical measurements are necessary in many facets of the developing endocrine disrupting environmental programs. The screening phase will likely be conducted with high-throughput, specific tests. The development of regulations, monitoring and remediation may be done with more conventional techniques, where suitable, and new technology where necessary. Analytical measurements have been developed for many of these compounds using existing technology. In many cases, the performance of EPA methods can be significantly improved with modifications that take advantage of newer instrument designs and ancillary techniques.

This work summarizes the performance of existing US EPA methods for low detection limits and confirmatory analysis. Method enhancements and new technology will be evaluated for applicability to endocrine disrupting compounds.

INTRODUCTION

Endocrine disrupting compounds are of global interest and several countries have generated lists of suspected compounds. Table 1 (from references 1-5) shows lists of compounds from several sources. Many of the compounds appear on several lists and may be considered more “suspect” than other compounds listed only once. The most extensive list is provided by the Japanese, with 68 chemicals listed. The largest category of chemicals is pesticides, representing approximately 50% of the chemicals listed. Metals are represented 7 times on the list and the exact species of the metal may influence its ability to disrupt the endocrine system. The problem is global, and although very few of the analytes are volatile, the movement of chemicals around the world makes this a concern in every country. Chemical producers of materials on the suspect list are distributed in at least 41 countries, reinforcing the global perspective.[6]

Table 1. Suspected Endocrine Disrupting Compounds (From references 1-5)

Compound	Type[6]	EPA	CDC	WWF	EU	JEA	PRC
2,4,5-T	H		X	X	X	X	X
2,4-D	H	X	X	X	X	X	
2,4-Dichlorophenol	C			X		X	
2-Acetylaminofluorene	C	X					
3,3’,4,4’,5,5’-Hexachlorobiphenyl	PCB	X					
3,3’,4,4’,5-Pentachlorobiphenyl	PCB	X					
3,3’,4,4’-Tetrachlorobiphenyl	PCB	X					
Acenaphthene	C	X					
Acrylonitrile	I						X
Alachlor	H	X	X	X		X	
Aldicarb	N,I		X	X		X	

Compound	Type[6]	EPA	CDC	WWF	EU	JEA	PRC
Aldrin	I	X			X	X	X
Alkyl phenols (C5-C9)	B			X	X	X	
Allethrin	I	X					
alpha-BHC/HCH	I	X					X
Amitrole	H		X	X	X	X	
Anthracene	C	X					
Arsenic	M	X					X
Atrazine	H	X	X	X	X	X	
Benomyl	F		X	X		X	
Benz(a)anthracene	C	X					
Benzo(a)pyrene	C	X		X		X	
Benzo(b)fluoranthene	C	X					
Benzo(k)fluoranthene	C	X					
Benzophenone	C			X		X	
Benzylphenol	B				X		
Beta-HCH/BHC	I	X	X	X	X		X
Bisphenol-A	C	X	X	X		X	
Butyl benzyl phthalate	C	X	X	X	X	X	
Butylated hydroxyanisole (BHA)	C	X					
Butylated hydroxytoluene (BHT)	C	X					
Cadmium	M	X	X	X			
Carbaryl	I		X	X	X	X	
Chlordane	I	X	X	X	X	X	X
Chlordimeform	I						X
Chloropicrin	B						X
Chlorothalonil	F	X					
Chlorpyrifos/Dursban	I	X					
Chrysene	C	X					
Copper	M	X					
Cyanide	C						X
Cyhexatin	I	X					X
Cypermethrin	I			X		X	

Compound	Type[6]	EPA	CDC	WWF	EU	JEA	PRC
DBCP	N,I		X	X		X	X
DBP	C	X		X	X	X	
DCHP	C			X		X	
DDT/DDE/DDD	I	X	X	X	X	X	X
DEHP	C			X	X	X	
Demeton	I						X
DEP	C			X		X	
DHP	C			X		X	
Dicofol/Kelthane	I,A		X	X	X	X	
Dieldrin	I	X	X	X	X	X	X
Diethylhexyl adipate	C			X		X	
Dimethyl mercury	C	X					
Dinoseb	H, I						X
Dioxin*	C		X	X	X	X	
DPP	C			X		X	
DprP	C			X		X	
EDB	I						X
Endosulfan	I	X	X	X	X	X	
Endrin	I	X				X	X
Esfenvalerate	I			X		X	
Fenarimol	F				X		
Fenvalerate	I			X		X	
Fluoroacetamide	I						X
Flutamid					X		
Heptachlor	I	X	X	X		X	X
Heptachlor epoxide(heptachlor metabolite)	I		X	X		X	
Hexachlorobenzene	F		X	X	X	X	X
Hexachlorocyclohexane	I					X	
Indeno(1,2,3-cd)pyrene	C	X					
Kepone	I			X	X	X	
Lead	M	X	X	X			
Lindane(gamma-HCH/BHC)	I	X	X	X			X

Compound	Type[6]	EPA	CDC	WWF	EU	JEA	PRC
Malathion	I			X	X	X	
Mancozeb/Maneb	F		X	X	X	X	
Manganese	M	X					cyhexa
Mercury	M	X	X	X			X
Methomyl	I		X	X		X	
Methoxychlor	I		X	X	X	X	
Metolachlor	H	X					
Metribuzin	H		X	X	X	X	
Metriram-complyx	F		X	X	X	X	
Mirex	I		X	X		X	
n-Butyl benzene	C			X		X	
Nitrofen	H		X	X	X	X	
Nonylphenols	C	X	X		X	X	
Octachlorostyrene	C			X		X	
Octaphenol					X	X	
Oxychlordane(chlordane metabolite)	I	X	X	X		X	
Parathion (ethyl)	I		X	X	X	X	
PBBs	C			X?	X	X	X
PCBs	C	X	X	X	X	X	X
Pentachloronitrobenzene	F	X					
Pentachlorophenol	C,H	X	X	X		X	X
Permethrin	I	X		X		X	
Phenanthrene	C	X					
p-Nitrotoluene	C			X		X	
Polycarbonates							
Pyrene	C	X					
Pyrethroids (synthetic)	I		X	X			
Quinalphos					X		
Simizine	H	X				X	
Styrenes (polymer, not monomer)	C		X	X?		X	
Styrol	C				X		
Thiram	B				X		

Compound	Type[6]	EPA	CDC	WWF	EU	JEA	PRC
Tin	M	X					
Toxaphene	I		X	X	X	X	
trans-nonachlor	I	X	X	X	X	X	
Tributyl tin oxide(or chloride)	B,F,C	X	X	X		X	
Trifluralin	H	X	X	X	X	X	
Triphenyl tin acetate	B	X				X	
Triphenyl tin hydroxide	B	X					
Vinclozolin	I	X		X	X	X	
Zineb	F		X	X	X	X	
Ziram	F		X	X	X	X	
Total		**58**	**45**	**67**	**42**	**68**	**27**

* 2,3,7,8-TCDD, Dioxins, & Furans

EPA = Environmental Protection Agency
CDC = Centers for Disease Control
WWF = World Wildlife Fund, Canada
EU = European Union
JEA = Japan Environmental Agency
PRC = People's Republic of China Toxic Chemicals Banned or Severely Restricted
B = Biocide
I = Insecticide
H = Herbicide
N = Nematocide
F = Fungacide
C = Industrial Organic Chemical
M = Metal
PCB = Specific PCB isomer
# = No commercial use; compound is a degradation product or impurity of other chemicals
A = Acaricide

Some of the chemicals listed are persistent in the environment and even if production were stopped would continue to require monitoring for years. Persistent organic chemicals are listed in reference 7. Metals do not degrade, although the species may change, and may pose a significant on-going exposure for many years.

Many of the chemicals listed in the suspect list have been regulated in existing environmental programs. Although the limits are generally based on toxicological concerns, lower levels may be measured using the same methodology in many cases. US regulatory limits for water (generally the lowest regulatory limits) are listed for 28 of the chemicals. The EPA method detection limits are adequate, in many cases for the existing requirements and for somewhat lower detection requirements, by a factor of ten. If more than a factor of ten is required then additional method development or new technologies will be required.

METHOD ENHANCEMENTS

In some cases extensions of existing methods can improve the detection limits significantly. Some of these changes have been codified into EPA methods, and many more are possible with the move towards a performance-based measurement system. We will discuss four method improvements that can provide better detection limits that may be useful in future endocrine disruptor analysis work. The first is improvement in GC/MS detection limits for toxaphene using large volume injection. The second is improvement in mercury detection limits using amalgamation (incorporated in the recently released EPA method 1631). The third and fourth improvements are centered around inductively coupled plasma mass spectrometry (ICP-MS). Preconcentration coupled with

ICP-MS can remove difficult matrices and enhance of detection limits. Alternatively, the new technology of a dynamic reaction cell coupled with ICP-MS can remove interferences that inhibit detection capability. This technique can be extended to the analysis of metal species.

GC/MS Extension

Generally the determination of multicomponent analytes such as toxaphene, chlordane, and alachlors at low concentration can be challenging because the response is distributed among many peaks (multicomponent analytes). Gas chromatography with an electron capture detector has been the method of choice (EPA method 608) because of the sensitivity and specificity provided by the detector. The detection limit listed in the method is 0.24 µg/L. There are advantages to measuring this analyte with GC/MS, including reduction in additional analyses required for confirmation, and additional identification information in the structural fragment patterns. However, the detection limit for toxaphene listed in the EPA semivolatile GC/MS method is poorer at 1 µg/L. Using newer quadrupole technology and large volume injection of 50 µL rather than 1 µL it is possible to improve the detection limit to 0.027 µg/L with selected ion recording and 0.076 µg/L using full scanning.[8] This detection limit is well below the drinking water compliance limit of 3 µg/L and leaves room for lower levels to be measured with confidence. Routine analyses can be performed very cost effectively in a GC/MS analysis with a large suite of analytes and built-in confirmation step.

Mercury Analysis

Mercury analysis at ultratrace concentration has become of concern in recent years because of the global dispersion of the pollutant and its tendency to bioaccumulate. The EPA has investigated several enhancements to existing methodology and developed a method using clean sample collection and handling coupled with a preconcentration step before the measurement (EPA method 1631). Table 2 summarizes the techniques available for mercury measurement.[9] Mercury measurement is approaching background levels and the determination of much lower levels will require extreme care in all aspects of collection and analysis.

Table 2. Mercury Measurement Technique Detection Limits

Technique	Detection Limit (mg/L)
ICP-OES	8
ICP-MS	0.2
Flow Injection AAS	0.1
Flow Injection FIMS (dedicated analyzer)	0.004
Flow Injection FIMS with amalgamation	0.0002
Flow Injection Amalgamation ICP-MS	0.0002

Typical routine analyses in drinking water for compliance with 2 µg/L limits can be satisfactorily performed with ICP-MS or with atomic absorption techniques. For ultratrace analysis, preconcentration will enhance the detection limit capability of atomic absorption and ICP-MS.

ICP-MS Technology

ICP-MS technology can provide an economical analysis of many elements at ultratrace concentrations in a single run. In addition, ICP-MS can easily be coupled to a separation technique, such as HPLC to provide separation of metal species prior to measurement. Isobaric interferences are interferences that occur at the same mass/charge ratio as the analyte of interest. For many elements it is possible to choose an alternative mass for observation, but for monoisotopic elements, such as arsenic, this is not an option. For some elements a less sensitive mass may be used, but this is not optimum if the best detection limits are desired. Elemental correction equations and higher resolution mass spectrometers have also been useful.

In some heavy matrices, such as seawater, the best detection limits can be difficult to achieve because dilution may be required for the instrument to analyze the matrix for long periods of time. Preconcentration can isolate the elements of interest from the matrix and enhance their concentration in the eluent introduced into the instrument. Willie, et al.[10] used flow injection coupled with concentration on an iminodiacetic acid resin to isolate Cu, Ni, Zn, Mn, Co, Pb, Cd, and V from seawater. They demonstrated detection limits of less than 10 pg/mL. This is a

variation of EPA method 200.10/1640, which specifies the preconcentration of Cd, Cu, Pb, and Ni using on-line chelation. The detection limits are lower than those generally obtained in simple matrices without preconcentration. Method 1640 specifies clean sample collection and handling to limit contamination of the sample.

An alternate technique for removing isobaric interferences is to use reaction cell technology. The ELAN 6100 DRC uses a dynamic reaction cell. The dynamic reaction cell is an enclosed rf-only multipole that can be pressurized with a reactive gas. The gas can react with the analyte to create a polyatomic ion, which is not interfered or converts the isobar to a different ion, which does not interfere. The specific chemistry is dependent on the nature and density of the reactive gas and the electrical fields within the cell. Arsenic is a candidate for detection limit improvement using this technology. It is monoisotopic, with one mass at 75 amu. More than 50 mg/L Cl will cause measurable ArCl interference at mass 75. Although elemental equations and other compensation techniques can reduce the problem, removal of the interference may prove advantageous. Preliminary work used 40% hydrogen in helium as the reactant gas.[11] The proposed reactions are as follows:

- $ArCl^+ + H_2 \rightarrow ArH_2^+ + HCl$
- $ArH_2^+ + H_2 \rightarrow H_3^+ + Ar$

Detection limits measured under these conditions for arsenic in 1g/L NaCl are 4 ng/L. This restores the detection limit capability to that seen in a simple drinking water matrix. The implications for achieving low detection limits in the wide variety of matrices that must be examined for endocrine disrupting analytes is significant. In addition, this technique may allow speciated analysis in difficult matrices or buffers used in the HPLC process to be more easily optimized.

SUMMARY

The full scope of endocrine disrupting compounds that may require monitoring and remediation are not yet known, but we can make some reasonable assumptions about the tentative list. Measurement capabilities for many of the compounds and elements have been developed over the years as environmental programs developed and noted toxicity levels. Many of the methods that exist can be enhanced by the use of newer technology and preconcentration techniques. New types of technology, such as the dynamic reaction cell can extend the application of a technique to additional matrices. In the future additional matrices may require analysis for potential contamination or as a source of exposure. Cost effective measurements will become more critical as the list of analytes becomes better defined and regulations for monitoring are promulgated. Implementation of a performance-based measurement system will remain a key issue in allowing timely access to modified methods and new technology.

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PERFORMANCE OF A NEXT GENERATION VIAL AUTOSAMPLER FOR THE ANALYSIS OF VOCS IN WATER MATRICES

Eric Heggs
Tekmar-Dohrmann, 7143 East Kemper Road, Cincinnati, OH 45249

In today's laboratories, increased efficiency and productivity is of extreme importance. Equally important is the ability to automate analyses without sacrificing sample integrity or data quality. A new vial autosampler, the AQUAtek 70, has been developed to fully automate purge and trap analysis of water samples in accordance with current EPA methods for volatile analysis.

The AQUAtek 70 Liquid Autosampler is a 70 position autosampler that can handle water and wastewater samples of all types including particulate laden samples. The AQUAtek 70 offers improved data quality with automatic sample volume measurement and automatic standard addition. A high temperature OptiRinse system virtually eliminates carryover and improves productivity. Research will be presented demonstrating the instrument's ability to transfer sample aliquots with the addition of internal standard or surrogate solutions. Data will be evaluated for linearity, precision, and accuracy. In addition, the instrument's sample pathway will be evaluated for carryover, inertness, and reliability."

MAKING USE OF DISSOLVED HYDROGEN ANALYSIS EASIER: A NEW SAMPLING PROCEDURE, THOROUGH HOLDTIME STUDIES AND NEW QUALITY ASSURANCE AND CONTROL MEASURES

Patrick McLoughlin
Microseeps, Inc., 220 William Pitt Way, Pittsburgh, PA 15238

Monitoring the concentration of dissolved Hydrogen has been suggested for its utility in delineating the ‘redox’ zones, in assessing the potential for the reductive dechlorination of chlorinated solvents and in assessing the potential for the reductive biodegradation of methyl-tert-butyl ether (MTBE). The idea has gained widespread acceptance but dissolved hydrogen concentrations are rarely monitored. We’ve carried out a set of studies designed to make the use of dissolved hydrogen analyses more attractive. We have developed a new sampling apparatus which is more convenient, faster and more reliable than the typical ‘bubble strip’ sampler. We have developed sampling procedures which are dependable, have a very clear, detailed and illustrated instruction set, are easier to use and, most importantly, reduce sampling time. We have characterized the hold time limits for dissolved hydrogen analysis and altered our methods to comfortably achieve appropriate MDLs. Through our extensive experience with dissolved gas sampling and analyses, we have developed quality assurance and quality control steps that provide additional data quality assessment at comparable cost.

QUANTITATIVE ANALYSIS OF THE CHEMICAL WARFARE AGENT VX IN CAUSTIC WASTESTREAMS GENERATED DURING DEMILITARIZATION OPERATIONS

Kevin Morrissey
EAI Corporation, 1308 Continental Drive, Suite J, Abingdon, MD 21009

The decision to utilize chemical neutralization for Stage 1 destruction of the VX stockpile at Newport, IN requires that a reliable method be available to screen the resulting caustic wastestream for residual VX. This method should be rugged, suitable for use in a plant environment, and amenable to automation. This work reports on the efforts to develop, optimize, and validate such a method.

The use of solid phase extraction, followed by GC/MSD, for the anaysis of VX in caustic wastestreams was optimized, validated, and then applied to the analysis of multiple small scale (2 liter) reactor samples. The sample preparation method was optimized with respect to solid phase sorbent type, wash solution, and elution solvent. The chromatography was optimized with respect to injection solvent, vial type, injection parameters, and oven temperature profile.

Precision and accuracy experiments using actual reactor samples were performed at 10 and 20 ng/g VX. The overall precision (as percent relative standard deviation) was determined to be 13%. The overall accuracy (as percent recovery) was determined to be 85%. The overall method limit of detection was determined to be 4 ng/g VX. Additional results and method details will be reported.

FREEZE-DRYING OF SEDIMENTS TO ACHIEVE RISK-BASED DETECTION LEVELS FOR PCB CONGENERS, POLYNUCLEAR AROMATIC HYDROCARBONS (PAHS), AND METALS

Susan D. Chapnick and Nancy C. Rothman, Ph.D.
New Environmental Horizons, Inc., 34 Pheasant Run Drive, Skillman, NJ 08558
Peter Kane
Woods Hole Group Environmental Laboratories, 375 Paramount Drive, Suite B, Raynham, MA 02767
Charles A. Menzie
Menzie-Cura & Associates, Inc., One Courthouse Lane, Chelmsford, MA 01824

ABSTRACT
A new approach to the preparation of sediments for environmental analysis of chemicals of concern, in support of risk assessments, has been successfully implemented at several sites in Massachusetts under the direction of the EPA Region I QA Branch. This approach involves the freeze-drying of sediments prior to extraction or digestion for analysis of PCB congeners, PAHs, and metals. High percent moisture (low percent solids) content in sediments makes it difficult to achieve contaminant detection levels low enough to meet risk-based data quality objectives. When sample-specific detection limits are calculated, the required dry-weight conversion raises the level of detection in non-detected compounds. These raised reporting limits often do not meet the low-level concentrations needed for human health and ecological risk assessments. In addition, EPA Region I Data Validation protocols require the rejection of non-detected results from samples with less than 30% solids. This EPA requirement can result in significant data gaps for sediment data needed to support risk assessment. This study presents results that support the use of freeze-drying as a viable tool in producing usable data for risk decisions. The study included both native sediment and standard reference material (SRM). Native sediment samples collected at a site in Massachusetts were prepared in duplicate. The percent solids in the 15 native sediment samples ranged from 7.2 to 27%. The percent solids after freeze-drying ranged from 42 to 97%. These results achieved the first goal of attaining percent solids >30% to eliminate the potential data losses due to rejections following EPA Region I data validation guidelines. To assess the second goal of determining effects on accuracy of chemical measurements for PCB congeners, PAHs, and metals in freeze-dried vs. non-freeze-dried sediments, a SRM for the compounds of interest was re-constituted to match the native sediment percent solids and then freeze-dried and analyzed in duplicate. The SRM was also prepared and analyzed, in duplicate, without treatment (as-received from the vendor). Results of the SRM and native sediment samples showed acceptable comparability (criterion set at a relative percent difference of $\leq$ 20%) of detected results between freeze-dried and non-freeze dried samples for 18 PCB congeners, PAHs, and target analyte list (TAL) metals. In conclusion, freeze-drying reduces moisture content

in sediments, thereby making risk-based reporting limits attainable for non-volatile chemical contaminants and eliminating the need to reject non-detected results.

INTRODUCTION

High percent moisture (low percent solids) content of sediments often makes it difficult to achieve contaminant detection levels low enough to meet risk-based Data Quality Objectives. When sample-specific detection limits are calculated, the required dry-weight conversion raises the level of detection in non-detected compounds. These raised detection levels often do not meet the low-level (risk-based) concentrations needed for human health and ecological risk assessments. In addition, EPA Region I Data Validation protocols require the rejection of non-detected results from samples with less than 30% solids. This EPA requirement can result in significant data gaps for sediment data needed to support risk assessment. This study examines the use of freeze-drying as a viable tool in producing usable data for risk decisions through increasing the percent solids of the sediments prior to extraction and analysis; thereby, decreasing the achievable levels of detection in this media.

The goals of the project were:

1. To meet the low project-specific reporting limits required to support ecological risk assessment for polyaromatic hydrocarbons (PAHs), PCB Congeners, and metals in sediments.
2. To obtain percent solids in sediment samples at levels greater than 30% so that the non-detected results would be usable under EPA Region I Data Validation guidelines.

EXPERIMENTAL DESIGN

1. Fifteen sediment samples were collected from a site in Massachusetts (July 1999). The percent solids in the native or “as received” sediment samples were measured.
2. Standard Reference Material (SRM) 1941A from NIST, Organics in Marine Sediment, was used for PAHs and PCB Congeners and SRM No. PPS-46 from ERA was used for metals. The SRMs were reconstituted with laboratory analyte-free water to a percent solids < 30%, to mimic the percent solids observed in the natural sediments.
3. The sediments and two aliquots each of the reconstituted SRMs were freeze-dried using a Hull 8FS12C Freeze-drying apparatus with the following protocol:
   - 3.1 An 8 oz. jar was filled to no more than half way with the sediment or SRM. The lid was placed on the jar loosely to allow for air and water vapor to escape.
   - 3.2 Samples were placed onto the pre-cool shelf at - 45°C for four hours.
   - 3.3 Samples were brought to a temperature of 28 ± 3°C for a time of 78 hours. The freeze drying apparatus was brought to a pressure of 150 millitorr for the duration of the process.
   - 3.4 Once the samples were at an acceptable dryness, they were removed from the unit and stored at 4°C until sample preparation (extraction or digestion) was performed.
4. The percent solids of the freeze-dried sediments and treated SRMs were determined. The fifteen freeze-dried sediments, a native sediment, the duplicate treated SRMs, and duplicate untreated or “as received” SRMs were prepared for analysis as follows: SW-846 Method 3545, Accelerated Solvent Extraction, for PAHs; EPA Method 1668, modified Soxhlet extraction, for PCB Congeners; and SW-846 Method 3050, Acid Digestion of Sediments, Sludges, and Soils, for metals.
5. Samples were analyzed using EPA SW846 Method 8270C for the PAHs, SW-846 Methods 6010B and 7000-series methods for metals, and EPA Method 1668 for PCB Congeners.

RESULTS AND CONCLUSIONS

During the sampling of these sediments, all efforts were made to minimize entrained water to the extent that a dewatering procedure, based upon EPA Region I Sediment Sampling Guidance, was used to collect the sediments. Table 1 shows a comparison of percent solids between the native sediments and the freeze-dried sediments. As this table indicates, the percent solids of the native sediments ranged from 7.2 to 27 % while the percent solids after freeze-drying ranged from 42 to 97%. For the types of sediments collected in this work, the dewatering procedure alone was not adequate for increasing the solids content of the samples above 30%. The increase in percent solids achieved by freeze-drying had the desired effect of decreasing the sample-specific reporting limits such that risk-based levels of detection were met for the compounds of interest. The reduction in the sample-specific reporting limits is illustrated in the following example:

Example: Sample-specific Reporting Limit for Naphthalene in Sample 4

$$\text{Concentration low instrument standard} \times \frac{\text{Final extract volume}}{\text{Wt. Sample extracted}} \times \frac{1}{(\%\text{solids}/100)} = \text{Sample-specific RL}$$

Native Sediment

$$10\ \text{ng/mL} \times \frac{2\ \text{mL}}{30.18\text{g}} \times \frac{1}{(8.8/100)} = 7.5\ \mu\text{g/Kg dry weight}$$

Freeze-dried Sediment

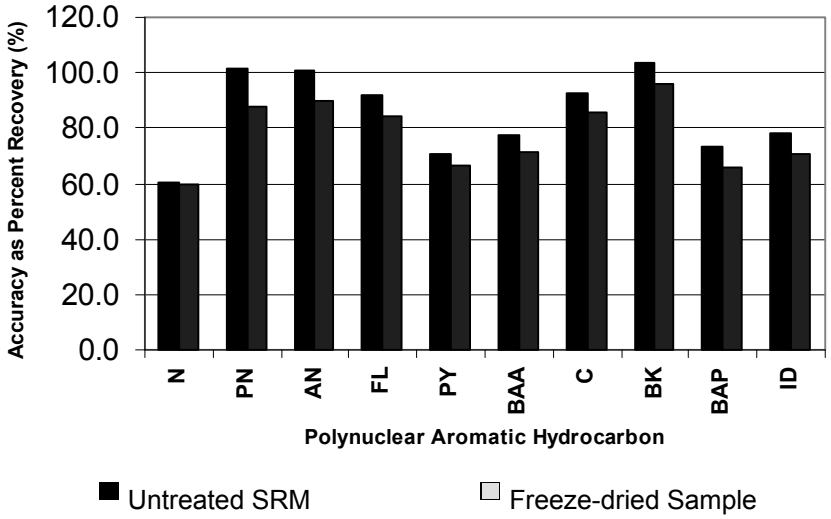
$$10\ \text{ng/mL} \times \frac{2\ \text{mL}}{30.18\text{g}} \times \frac{1}{(92/100)} = 0.72\ \mu\text{g/Kg dry weight}$$

Table 1. Native vs. Freeze-Dried Percent Solids in Sediments

Sample	Native Sediment % Solids	Freeze-Dried Sediment % Solids
1	13	67
2	14	84
3	27	79
4	8.8	92
5	24	87
6	11	97
7	10	55
8	7.2	42
9	17	78
10	10	61
11	18	88
12	24	68
13	23	78
14	22	79
15	15	81

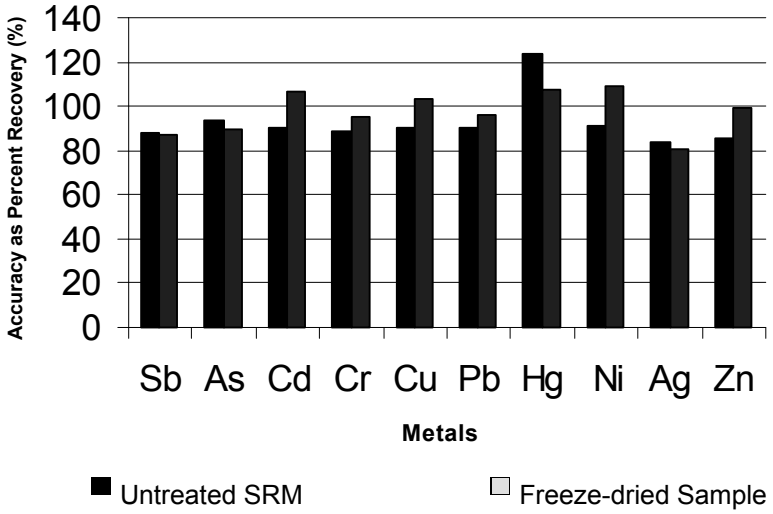
The increased percent solids allowed for the acceptance of non-detected results in these sediments following the data validation protocols of EPA Region I.

Figures 1 through 3 show a comparison of the untreated SRM and freeze-dried SRM for PAHs, metals, and PCB Congeners. These figures indicate that the accuracy of the PAH, metals, and PCB congener measurements was not adversely affected by the freeze-drying procedure. The paired results of the untreated and reconstituted/ freeze-dried SRM showed comparable results and acceptable recoveries for risk assessment needs.



Key to Polynuclear Aromatic Hydrocarbons:
N = Naphthalene
PN = Phenanthrene
AN = Anthracene
FL = Fluoranthene
PY = Pyrene
BAA = Benzo(a)anthracene
C = Chrysene
BK = Benzo(b)fluoranthene and Benzo(k)fluoranthene
BAP = Benzo(a)pyrene
ID = Indeno(1,2,3-cd)pyrene

Figure 1. Accuracy of Untreated and Freeze-Dried SRMs for PAHs



Key to Metal Analytes:
Sb = Antimony
As = Arsenic
Cd = Cadmium
Cr = Chromium
Cu = Copper
Pb = Lead
Hg = Mercury
Ni = Nickel
Ag = Silver
Zn = Zinc

Figure 2. Accuracy of Untreated and Freeze-Dried SRMs for Metals

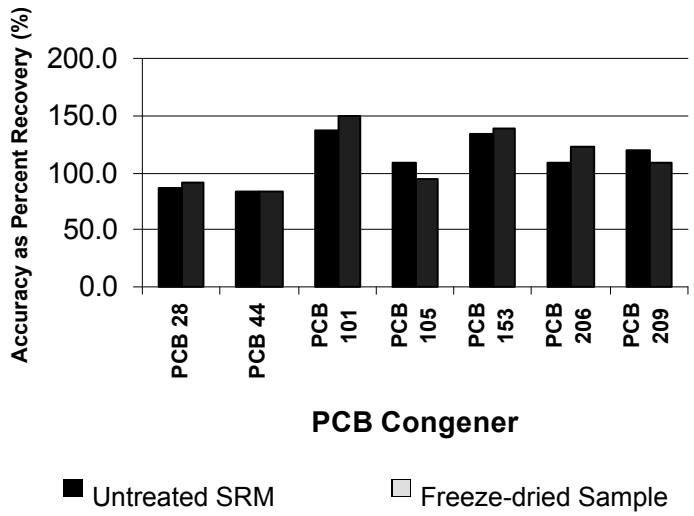


Figure 4 shows a comparison of the PAH results for a native sediment sample versus the results for the same sediment after freeze-drying. The overall concentration increase for several PAHs observed for the freeze-dried sediment may be due to an enhancement in the extraction efficiency for the freeze-dried aliquot. For PAH extraction, approximately 30g of sample is used. If the native sample contains 8.8% solids, only 2.64g of solids are actually extracted. The freeze-dried sediment, with percent solids increased to 92%, would allow 27.6g of solids to be extracted, thereby increasing the surface area, and possibly homogeneity of the sample, for solvent extraction.

Figure 3. Accuracy of Untreated and Freeze-Dried SRMs for PCB Congeners

SUMMARY

Freeze-drying of sediment samples has been shown to be an effective tool for increasing the solids content of the sediments without adversely affecting the non-volatile chemicals of concern within the samples. This technique can be applied to a wide range of matrices, for example plant tissue, where low solids content has the effect of raising the reporting limits for the chemicals of concern over risk-based criteria. For each batch of samples undergoing freeze-drying, a reconstituted SRM, if available, should be processed at the same time to serve as a batch quality control sample for the freeze-drying procedure. If an SRM is not available, a matrix spiked sample, may be used for quality control purposes. The freeze-drying procedure should not be used when evaluating "volatile" analytes such as Acid Volatile Sulfides and Simultaneously Extrac- ted Metals (AVS/SEM). In addition, caution should be used if metals speciation (e.g., Arsenic III vs. Arsenic V) is of interest since the freeze-drying process may cause a conversion from one species to another.

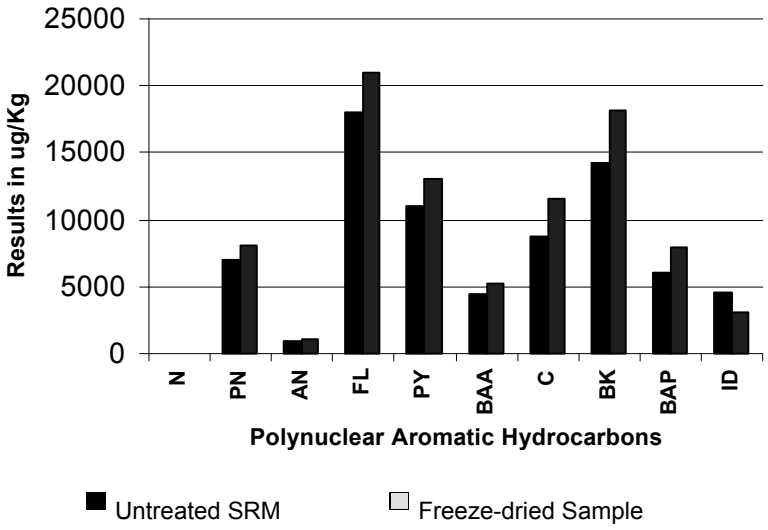


Figure 4. Results of Native Sediment Sample vs. Freeze-Dried Sediment Sample

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COMPARATIVE ANALYSIS OF SILCOSTEEL COATED SAMPLE PATHWAY AND ELECTROFORM NICKEL SAMPLE PATHWAY IN THE TEKMAR 3100 SAMPLE CONCENTRATOR

Mark Krigbaum, Glynda Smith and Eric Thomas Heggs
Tekmar-Dohrmann, 7143 East Kemper Road, Cincinnati, OH 45249

INTRODUCTION

The Tekmar 3100 Sample Concentrator represents an extension of the 3000 Purge and Trap product line. Silcosteel tubing and Silcosteel-treated sample fittings are used throughout the sample pathway. Silcosteel treatment involves a process that shields the active surfaces of metal. A thin, silicon-based coating is applied to the metal surface, which keeps analytes from adsorbing onto active sites on the metal. As a result, there is enhanced inertness, corrosion resistance, and reduced adsorption. The 3100 Sample Concentrator also features improved temperature uniformity of the heated sample pathway, which reduces carryover, condensation and adsorption. Prior to the introduction of Silcosteel, the sample pathway consisted of electroform nickel and fittings constructed with electroless nickel plating. Difficulties can occur in the analysis of thermally labile analytes, high boiling compounds, flavor volatile organics, and some environmental compounds such as 1,1,2,2-tetrachloro-ethane. These compounds are targeted for evaluation because many of them are prone to breaking down and adsorbing onto active metal surfaces. In this paper, the results of a comparison study between samples evaluated using a Silcosteel sample pathway and an electroform nickel sample pathway will be presented and discussed.

EXPERIMENTAL

Instrumental Parameters

Table 1 describes the Purge and Trap Conditions used for the analyses